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The Uniformity of Substitution During the Emulsion Xanthation of Cellulose and the Solution Properties of the Corresponding Diethylacetamide Derivatives

Richard Henry Cornell

June, 1960

THE UNIFORMITY OF SUBSTITUTION DURING THE EMULSION XANTHATION OF CELLULOSE AND THE SOLUTION PROPERTIES OF THE CORRESPONDING DIETHYLACETAMIDE DERIVATIVES

A thesis submitted by

Richard Henry Cornell

A.B. 1953, Colgate University
M.S. 1955, Lawrence College

in partial fulfillment of the requirements
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PRESENTATION OF THE PROBLEM

> "The distribution of the substituents with regard to the length of the macromolecules has hitherto only been studied casually in connection with investigations on the polymolecularity of cellulose or its derivatives."
>
> Timell and Purves (1)

Commercial cellulose xanthate has an average of one xanthate group per two glucose units. This does not infer, however, that the xanthate groups are uniformly distributed upon all cellulose chains. The heterogeneous nature of the reaction system would suggest that this is not the case. If the reaction were principally molecular in nature, the distribution would presumably be uniform. On the other hand, if the reaction were micellar, the distribution would be expected to be somewhat less than uniform. The extent of the nonuniformity depends upon the relative reactivity of the amorphous regions as opposed to the crystallite regions.

There are some indications in the literature (2-8) that the shorter cellulose chains consume larger quantities of carbon disulfide than the longer chains. If such is the case and the longer chains are not sufficiently xanthated, difficulties in subsequent processing might be anticipated (9, 10). There is, however, other evidence indicating that substitution should occur quite uniformly (7, 8).

The xanthate groups in cellulose xanthate are quite unstable, even in an alkaline medium. Redistribution (transesterification) readily occurs, resulting in a more uniform distribution than that existing in the original xanthate (2, 5, 6).

This investigation is concerned with the uniformity in substitution for viscose prepared by the emulsion xanthation technique and the important factors believed to influence the uniformity, namely, the degree of substitution and the time of xanthation. Such information has resulted in a further understanding of the nature of the xanthation reaction and an estimation of the uniformity to be expected under various conditions.

In the course of this investigation, considerable information pertaining to the solution properties of the diethylacetamide derivative of cellulose xanthate (DAX) was obtained. No data of this nature have previously been published.

For reason of clarity, the presentation of these two phases of the work have been separated as follows:

Part I. The Uniformity of Substitution during Emulsion Xanthation of Cellulose.

Part II. The Solution Properties of Diethylacetamide Cellulose Xanthate in Dimethyl Sulfoxide.

UNIFORMITY OF SUBSTITUTION DURING EMULSION XANTHATION OF CELLULOSE

INTRODUCTION

CHEMISTRY OF THE VISCOSE PROCESS

The conversion of cellulose to cellulose xanthate may be represented schematically as follows:

$$\text{Cellulose} \xrightarrow[18\%\,NaOH]{\text{Steeping}} \text{Alkali Cellulose I} \xrightarrow{\text{Aging}} \text{Low D.P. Alkali Cellulose I}$$

$$\xrightarrow[CS_2]{\text{Xanthation}} \underset{(\underline{ca}.\ 1CS_2:2C_6H_{10}O_5)}{\text{Cellulose Xanthate}} \xrightarrow{\text{Dissolving}} \underset{\substack{6\text{-}10\%\ \text{Cellulose}\\ 4\text{-}8\%\ NaOH}}{\text{Viscose}} \xrightarrow{\text{Ripening}} \underset{(\underline{ca}.\ 1CS_2:3C_6H_{10}O_5)}{\text{Viscose}}$$

In the presence of water, sodium hydroxide forms an addition complex with cellulose as follows:

$$\text{Rcell-OH} + \text{NaOH} \longrightarrow \text{Rcell-OH}\cdot\text{NaOH}$$

Under the usual steeping conditions the cellulose swells and absorbs water and alkali to form alkali cellulose I ($C_6H_{10}O_5 \cdot NaOH \cdot 3H_2O$).

Following pressing and shredding, the alkali cellulose, aged in the presence of air, undergoes oxidative degradation. The practicable limits for the degree of polymerization (D.P.) following aging will be 200-400.

Alkali cellulose, when treated with carbon disulfide, forms the sodium salt of cellulose dithiocarbonate, commonly referred to as cellulose xanthate.

$$\text{Rcell-OH}\cdot\text{NaOH} + CS_2 \longrightarrow \text{Rcell-OCS}_2\text{Na} + H_2O$$

Side reactions, occurring during xanthation, include both secondary reactions of the xanthate and reaction between the carbon disulfide

and sodium hydroxide. Secondary products arising from the reactions include sodium trithiocarbonate (Na_2CS_3), sodium sulfide (Na_2S), sodium hydrosulfide (NaSH), and sodium carbonate (Na_2CO_3).

Ripening, or decomposition, of the xanthate occurs as a result of its inherent instability in alkaline solution. Decomposition by either hydrolysis or saponification may predominate depending upon the conditions. The probable reaction mechanisms are represented as follows:

Hydrolysis: $\text{Rcell-OCS}_2\text{Na} + \text{H}_2\text{O} \longrightarrow \text{Rcell-OCS}_2\text{H} + \text{NaOH}$

$\text{Rcell-OCS}_2\text{H} \longrightarrow \text{Rcell-OH} + \text{CS}_2$

Saponification: $\text{Rcell-OCS}_2\text{Na} + \text{H}_2\text{O} \longrightarrow \text{Rcell-OH} + \text{NaCS}_2\text{OH}$

$\text{NaCS}_2\text{OH} + 5\text{NaOH} \longrightarrow 2\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}$

In the case of ordinary commercial viscose, approximately 15-20% of the decomposition results from saponification (11). Increasing the amount of alkali in the system will increase this percentage. The subsequent loss of dithiocarbonate groups leads directly to the appearance of certain by-products--principally sodium trithiocarbonate (Na_2CS_3), with somewhat lesser amounts of sodium sulfide (Na_2S), sodium polysulfide (Na_2S_2), sodium thiosulfate ($Na_2S_2O_3$), and sodium carbonate (Na_2CO_3).

MECHANISM OF XANTHATION

Cellulose reactions may be classified broadly as either homogeneous or heterogeneous. In the case of a homogeneous reaction, e.g., the etherification in quaternary ammonium bases, the substituents are uniformly distributed throughout the product. Heterogeneous reactions, on the other hand, yield products with somewhat lesser degree of uniformity.

Both the topochemical (micellar heterogeneous) and permutoid (quasihomogeneous) reactions have been suggested as the predominating mechanism during the xanthation of alkali cellulose. If the amorphous regions and surfaces of the cellulose crystallites react more rapidly than the interior of the crystallites, fractionation of the viscose or suitable derivatives of the viscose would exhibit varying degrees of substitution. On the other hand, no differences in substitution would be apparent if the reaction were homogeneous.

POSITION OF THE XANTHATE GROUP ON THE GLUCOSE UNIT

Considering the basic glucose unit, it is apparent that there are eight possible structures resulting from xanthation.

(a) Unsubstituted glucose unit
(b) Three mono-xanthates: substitution in the 2, 3, or 6 position
(c) Three di-xanthates: substitution in the 2, 3; 2, 6; or 3, 6 positions
(d) One tri-xanthate: substitution in the 2, 3, and 6 positions

Complete substitution is rarely achieved in actual practice. Lieser (12) has prepared the trixanthate by the dispersion of cellulose in tetraalkylammonium hydroxide. Freshly prepared viscose will, however, have a D.S. of 0.6-0.7, while the ripened viscose will have a D.S. of 0.3-0.5. Evidence supports the contention that the amounts of the di- and tri-xanthate are negligible in commercial xanthates (2, 13).

Of principal concern, therefore, are the three possible mono-xanthates. Lauer (14), by means of methylation studies, concluded that, for low degrees of substitution, reaction was at the 2- position. For higher degrees of substitution, reaction also took place at the 3- position. Chen, et al. (2) found random distribution between the

2-, 3-, and 6- positions. Purves, et al. (15, 16) have presented evidence that the xanthate groups appear to occupy the 3- and 6- positions.

VISCOSE RIPENING

The actual mechanism of dispersion of the xanthate in dilute alkali is open to question, i.e., whether it is micellar or molecular in character. Commercial viscose is assumed to be a mixture of micellar particles and individual molecules. More complete dispersion may be accomplished by dilution or increased substitution level.

Freshly prepared viscose readily decomposes by hydrolysis or saponification, resulting in a gradual increase in viscosity to a final point of complete gelation. Simultaneously, dithiocarbonate groups may pass between hydroxyl groups of the same or different chains (2, 5, 17). The net result of the decomposition and transesterification is a gradual loss of the xanthate groups and a more uniform distribution of the groups.

RELATED LITERATURE

DISTRIBUTION OF THE SUBSTITUENTS IN CELLULOSE DERIVATIVES (OTHER THAN CELLULOSE XANTHATE)

For a more complete understanding of the nature of the problem the reader is referred to the following examples from the literature for cellulose derivatives other than cellulose xanthate.

Yamamoto (18), Berl and Hefter (19), Rogovin and Glazman (20), and Brown and Purves (21) all obtained fractions differing in nitrogen content as a result of the fractionation of cellulose nitrate. Scherer and

Rouse (22), on the other hand, noted only slight variations. Abadie (23) and Timell (24) have taken into account the influence of nitrogen content on the measured intrinsic viscosity and thus have been able to relate substitution with chain length.

Clément and Rivière (25) reported a variation in acetyl content with D.P. for cellulose acetate. Scherer and Thompson (26) found increasing D.S. with decreasing D.P. for a commercial acetate. Lachs, et al. (27), however, reported a constant acetyl content for fractionated cellulose acetate.

Variations in D.S. were noted by Ushakov, et al. (28) for ethylcellulose, Steele and Pacsu (29) for a high-substituted methylcellulose, Timell and Purves (1) for low-substituted methylcelluloses, and Signer and Liechti (30) for a technical, water-soluble methylcellulose. Insignificant variations were reported by Okamura (31) for ethylcellulose, Scherer and McNeer (32) and Staudinger and Reinecke (33) for high-substituted ethylcellulose, and Glückman (34) for benzylcellulose.

DISTRIBUTION OF THE SUBSTITUENTS IN CELLULOSE XANTHATE

The inherent instability of cellulose xanthate precludes the direct use of common fractionation and analytical techniques for determining the xanthate group distribution. Stable derivatives, however, may be prepared by reaction with N-diethylchloroacetamide (35-37), methyl chloracetate (36, 37), chloracetonitrile (37), ethyl chloracetate (37), and perchloromethylmercaptan (37).

Fink, Stahn, and Matthes (36) fractionated the diethylacetamide derivative and determined the D.S. of the various fractions by nitrogen analysis. The authors concluded that there was a significant variation in D.S., although their data did not appear to substantiate this contention. It was also reported that two viscoses of similar D.S. and chain length may have decidedly different colloidal-chemical properties during ripening. This phenomenon was attributed to differences in location of the xanthate groups.

Scherer and Phillips (38) fractionated the diethylacetamide from an aqueous 2-chloroethanol solution. The D.P. of the fractions was determined from the intrinsic viscosity, using a value of 14.3×10^{-4} for the $\underline{k}_{\underline{m}}$ constant in the Staudinger relationship ($[\eta] = \underline{k}_{\underline{m}}$ D.P.). As will be shown in this thesis, the $\underline{k}_{\underline{m}}$ value is quite dependent upon substitution. The D.P. values reported by Scherer and Phillips are, therefore, subject to considerable question.

Chen, Montonna, and Grove (2) have reported results principally concerned with the structure and configuration of cellulose xanthate; however, the authors did fractionate both freshly prepared and ripened viscose by the addition of a saturated sodium chloride solution. Although somewhat inconclusive, the results indicated that in freshly prepared viscose the shorter chains were more highly xanthated. Viscose ripened four days, on the other hand, exhibited quite uniform distribution.

Serkov, et al. (5) concluded that the direct result of transesterification during ripening is a more uniform distribution of

xanthate groups. The authors prepared the diethylacetamide derivative and fractionally precipitated it from 2-chloroethanol. For both normal viscose and that prepared by the emulsion xanthation technique, the xanthate was found to be quite heterogeneous immediately after solution; but after sixteen hours the xanthate group distribution, as reflected by fractionation data, was quite homogeneous.

Recent unpublished work (39) indicated that no differences in substitution were apparent in fractions of the diethylacetamide derivative prepared from fresh commercial viscose. Differences were, however, found to exist in the freshly xanthated alkali cellulose crumbs. Whenever there was a dissolving step between preparation of the cellulose xanthate and preparation of the diethylacetamide derivative, D.S. differences between the fractions rapidly disappeared.

Schurz and Armbrüster (6)[a] have studied the course of ripening for viscose prepared by the emulsion xanthation technique. The diethylacetamide derivative was fractionated from a dimethyl sulfoxide solution. The relationship between gamma number (γ)[b], weight average D.P. ($D.P._w$), and intrinsic viscosity ($[\eta]$) was expressed by the following relationship:

$$[\eta] = (12.2-0.0783\gamma) \times 10^{-3} \; D.P._w$$

The data from which the authors derived this relationship are as yet unpublished. Freshly prepared viscose having a D.S. of 0.54 exhibited some degree of nonhomogeneity. The differential D.S. distribution curve was found to be almost identical with the D.P. distribution curve. The

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[a] Both the work of Schurz and Armbrüster (6) and Yamada and Mukoyama (40) were published while this thesis work was in progress.

[b] The gamma number is defined as the number of xanthate groups per 100 anhydroglucose units.

generalized form of the relationship between gamma number and D.P. was represented as follows:

$$\gamma = \gamma_o - kD.P.$$

where both γ_o and k are constants which decrease as ripening progresses. A completely uniform distribution is obtained when k becomes equal to zero.

Yamada and Mukoyama (40) fractionated viscose at various stages of xanthation using a fractional dissolution technique. The differential D.S. distribution curves at various time intervals indicated that maximum uniformity in substitution was achieved in two hours. The curve became somewhat broader for three hours xanthation. The authors based their explanation of this peculiar phenomenon on the hindered penetration due to xanthate swelling. The D.S. distribution was also determined during the dissolving and ripening steps by fractionation of the diethylacetamide derivative from both 2-chloroethanol and dimethyl sulfoxide. Fractionation of the derivative prepared from unripened viscose indicated a decrease in D.S. with succeeding fractions, which is contradictory to results reported by previous investigators (2, 5, 6).

CHARACTERIZATION OF THE COTTON LINTERS

Viscose-grade cotton linters were used throughout the experimental program. The linters (Type LMV, Lot 7102) were obtained through the courtesy of the Buckeye Cellulose Corporation. The linters were prepared for use by passing through a Wiley mill (40-mesh screen), and storing in covered containers until needed.

The linters were characterized by the analyses summarized in Table I.

TABLE I

ANALYSIS OF THE COTTON LINTERS

	Laboratory Data	Buckeye Data
Alpha-cellulose, % (41)	97.3	--
Soda soluble, % (42)	4.9	3.9
Ash, % (43)	0.07	--
Metals: Calcium, p.p.m. (44)	105	94
Iron, p.p.m. (45, 46)	9	10
Manganese, p.p.m. (45)	0.28	0.28
Viscosity: TAPPI Cupram, cp. (47)	14.2	--
TAPPI CED (0.5 g./100 ml.), cp. (48)	7.8	8.6
ACS Cupram (2.5 g./100 ml.), sec. (48)	9.0	10.7
$[\eta]_{CED}$ dl./g. (48)	4.8	--

A portion of the linters was nitrated according to the procedure of Bennett and Timell (49) (Appendix I). The average nitrogen content as determined by the method of Timell and Purves (1) (Appendix I) was 14.06%. The intrinsic viscosity calculated for the theoretical trinitrate according to the method of Lindsley and Frank (50) was 11.7 dl./g. The $D.P._n$ calculated according to the method of Immergut, et al. (51)[a] was 785. This checks quite well with the value of 750 calculated from the intrinsic viscosity in cupriethylenediamine (51)[b]. The $D.P._w$ calculated from the relationship given by Flory, et al. (52)[c] was 1135.

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[a] $(D.P._n)^{1.03} = 81.3\ [\eta]_T$

[b] $D.P._n = 156[\eta]_{CED}$

[c] $(D.P._w)^{1.01} = 104.0\ [\eta]_T$

The nitrate was fractionated from an acetone solution by the evaporation method of Timell (53). The fractionation data are summarized in Table II. The total amount of cellulose nitrate recovered was 95%. The viscosity data for the individual fractions are shown in Fig. 27 (Appendix II). The $D.P._n$ and $D.P._w$ values have been calculated in the same manner as described above from the theoretical trinitrate viscosities. The weighted average $D.P._n$ of 788 corresponded well with the value calculated for the unfractionated linters. The weighted average $D.P._w$ was 1147. The cumulative weight distribution and differential weight distribution curves are shown in Fig. 1.

TABLE II

FRACTIONATION DATA FOR NITRATED COTTON LINTERS

Fraction	Weight, %	Cumulative Weight, %	$[\eta]$,[a] dl./g.	$[\eta]_m$,[b] dl./g.	$D.P._n$[c]	$D.P._w$[d]
I	14.3	100.0	19.5	20.0	1320	1930
II	25.2	85.7	16.0	16.4	1085	1585
III	15.7	60.5	12.2	12.5	820	1210
IV	3.7	44.8	11.2	11.5	765	1115
V	4.1	41.1	10.6	10.9	725	1050
VI	2.0	37.0	8.65	8.87	585	862
VII	8.5	35.0	7.35	7.54	510	734
VIII	5.4	26.5	5.60	5.75	390	561
IX	15.6	21.1	4.20	4.31	295	422
X	5.5	5.5	3.50	3.59	250	352

[a] Intrinsic viscosities in ethyl acetate were determined at 20° ± 0.002°C. Kinetic energy corrections and shear correction were calculated to be less than 1% for this range of intrinsic viscosities.

[b] Calculated from Lindsley and Frank relationship (50).

[c] Calculated according to Immergut, et al. (51).

[d] Calculated according to Flory, et al. (52).

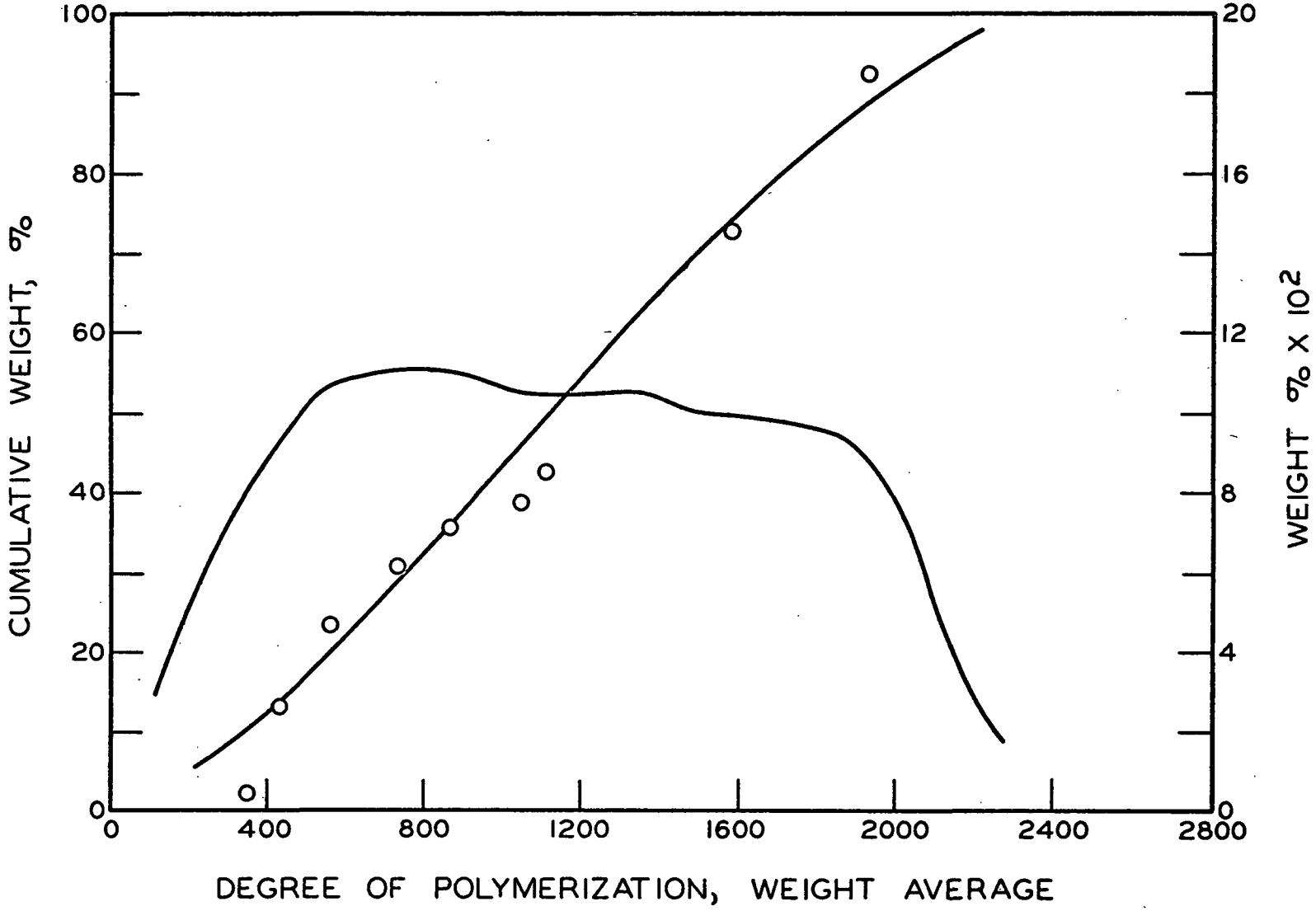

Figure 1. Integral and Differential Distribution Curves for Viscose-Grade Cotton Linters

EXPERIMENTAL PROCEDURES

VISCOSE PREPARATION (EMULSION XANTHATION)

The technique was basically that which has been described by Jayme (54, 55) with several slight modifications.

An amount of cotton linters corresponding to 8.54 grams o.d. was accurately weighed into a 500-ml. G.G.S. pyrex bottle. Sufficient distilled water (containing 6.431 g. glucose per liter) was added to bring the total weight of water to 125 grams. After one hour swelling, 12 mg. of abietic acid were added along with 200 ml. of 22.5% (by weight) sodium hydroxide and the desired amount of carbon disulfide.

Both the swelling in water (one hour) and the xanthation (six hours) were carried out at a constant rotation rate in a constant temperature bath (20° ± 0.02°C.). Apparatus for providing a constant rotation rate for three bottles (ca. 25 grams of cellulose) is shown in Fig. 2.

The total weight of viscose prepared per bottle was approximately 350 grams, depending upon the carbon disulfide addition. The corresponding cellulose concentration was about 2.4%; the sodium hydroxide concentration, about 13%.

CHEMICAL CHARACTERIZATION OF THE VISCOSE (Appendix I)

Total Sulfur (56)

The sulfur was transformed quantitatively to zinc sulfide by treatment with sodium zincate. The zinc sulfide was oxidized with a standard iodine solution and the unconsumed iodine was titrated with a standard sodium thiosulfate solution.

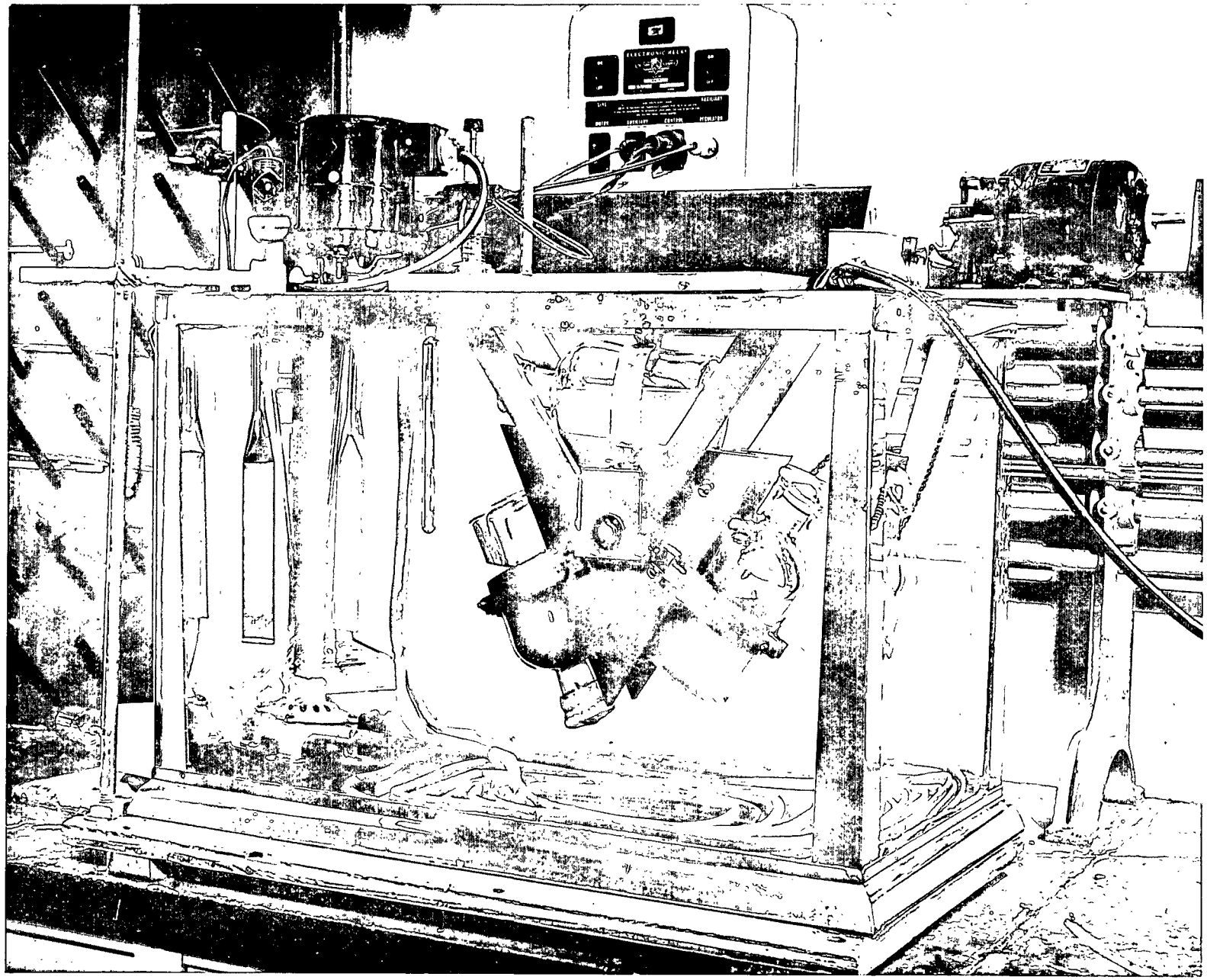

Figure 2. Rotation Apparatus for Viscose Preparation

Xanthate Sulfur (37, 57, 58)

The method was essentially that which has been described by Samuelson and Gärtner (57). The use of an ion-exchange resin (Amberlite IRA-400) enabled complete removal of the inorganic sulfur (i.e., primarily sodium sulfide and sodium trithiocarbonate), thereby eliminating the interfering sulfur. The xanthate sulfur was then determined in the same manner as described above for total sulfur.

By-product Sulfur

The by-product sulfur (sodium sulfide, sodium trithiocarbonate, and smaller amounts of sodium hydrosulfide) was determined from the difference between the total sulfur and the xanthate sulfur.

Total Alkali (59)

The total alkali was determined by ordinary acidimetric titration.

Free Alkali (60)

The free alkali includes all of the titratable alkali remaining after removal of the carbonate by the addition of a saturated barium chloride solution.

By-product NaOH

As with the by-product sulfur, this was calculated by difference. This value represents the alkali converted to the carbonate by reaction with the carbon disulfide.

PREPARATION OF DIETHYLCHLOROACETAMIDE (36, 61)

$$CH_2ClCOCl + (C_2H_5)_2NH \longrightarrow (C_2H_5)_2NCOCH_2Cl + HCl$$

One mole (113 grams) of chloracetyl chloride was dissolved in 280 ml. of purified dried ether. The solution was poured into a reflux condenser and maintained below 20°C. by immersion in an ice bath. To this solution were added two moles (146 grams) of diethylamine by means of a dropping funnel. Vigorous agitation was maintained. After the reaction was complete (two hours) the precipitated diethylamine hydrochloride was removed by filtering. The precipitate was washed thoroughly with ether. The ether was removed from the diethylchloroacetamide--ether mixture by distillation at atmospheric pressure. The product was purified by distillation at reduced pressure (29 in. vacuum). The boiling point was 120-126°C.

PREPARATION OF DIETHYLACETAMIDE CELLULOSE XANTHATE (DAX) (5, 6, 36, 38, 40)

$$Rcell\text{-}OCS_2Na + (C_2H_5)_2NCOCH_2Cl \longrightarrow Rcell\text{-}OCS_2\text{-}CH_2CON(C_2H_5)_2 + NaCl$$

Cellulose xanthate monomer weight = $162 + 98\underline{DS}$

Grams cellulose xanthate/gram original cellulose = $1 + 0.605\underline{DS}$

Grams diethylchloroacetamide/gram cellulose xanthate = $150\underline{DS}/(162 + 98\underline{DS})$

Grams DAX/gram original cellulose = $1 + 1.17\underline{DS}$

One hundred grams of viscose were diluted with 300 ml. of cold distilled water and neutralized with N/2 acetic acid to a phenolphthalein end point. To the neutral solution were added 25 ml. of diethylchloroacetamide. Complete addition of the acetamide groups was assured by maintaining vigorous agitation for at least fifteen minutes following

the addition of the diethylchloroacetamide. The precipitate was filtered, washed with distilled water, methanol-ether (1:1), and finally with anhydrous ether. The product was air dried overnight, dried in a vacuum desiccator, followed by drying at 50°C. (at atmospheric pressure).

FRACTIONATION OF THE DIETHYLACETAMIDE CELLULOSE XANTHATE

A one-per cent solution of the derivative was prepared in 70% 2-chloroethanol as recommended by Scherer and Phillips (38). Complete solution was accomplished by overnight shaking.

Precipitation was effected by means of successive additions of distilled water at room temperature. Each fraction was redissolved by raising the temperature to 35°C. Following slow cooling to room temperature, the fractions were isolated by centrifuging for one hour at 1500 r.p.m. This procedure was repeated until a suitable number of fractions were isolated. Each fraction was redissolved in 2-chloroethanol and reprecipitated by the addition of a large excess of distilled water. The fractions were washed with distilled water, methanol-ether (1:1), and anhydrous ether, followed by drying at 50°C.

DETERMINATION OF THE D.S. OF THE DAX DERIVATIVE

The conventional micro-Kjeldahl technique, as described by Timell and Purves (1), was found to be suitable for the determination of nitrogen in the diethylacetamide derivative. This procedure is described in Appendix I.

The nitrogen content in per cent ($\underline{N}$), is related to the D.S. of the diethylacetamide derivative as follows:

$$D.S. = 1.6214\underline{N}/(14.01-1.8933\underline{N})$$

VISCOSITY MEASUREMENTS

Reduced viscosities of the DAX derivatives were measured at 25° ± 0.02°C. in an Ubbelohde dilution viscometer with either 70% 2-chloroethanol (70ECH)[a] or 90% dimethyl sulfoxide (90DMSO) as the solvent.

The intrinsic viscosities, $[\eta]$, were obtained by extrapolation of the log $\eta_{sp}/\underline{c}$ versus $\underline{c}$ plots to zero concentration, according to the Martin equation (62).

$$\log(\eta_{sp}/\underline{c}) = \log[\eta] + k[\eta]\underline{c}$$

Kinetic energy corrections were found to be less than one per cent for all samples. Shear rates were calculated according to Kroeplin's (63) expression.

$$\underline{G} = 8\underline{V}/3\pi\underline{r}^3\underline{t}$$

where

$\underline{G}$ = the mean shear gradient, sec.$^{-1}$,

$\underline{V}$ = the volume of the bulb, 2.97 ml.,

$\underline{r}$ = the radius of the capillary, 0.0319 cm., and

$\underline{t}$ = the efflux time, sec.

For the DAX derivative in 90DMSO, the shear rates were 550 ± 25 sec.$^{-1}$. In 70ECH the shear rates were somewhat higher, 650 ± 25 sec.$^{-1}$. Extrapolation of the highest D.P. fraction to zero shear indicated that the maximum error due to the effect of shear would be of the order of 3%. Since most of the fractions have a D.P. below 2000, no correction for shear has been included in this work. Negligible shear correction has been indicated for cellulose nitrate below a D.P. of 2000. (51, 64, 65).

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[a] This solvent is commonly referred to in the literature as ethylene chlorohydrin. For this reason the designation 70ECH has been used throughout this work.

PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

EMULSION XANTHATION

Relationship between D.S. and Carbon Disulfide Addition

To enable preparation of viscoses of approximately known D.S. level, the relationship between D.S. and carbon disulfide addition was established. The other conditions as outlined in the section on Experimental Procedures were constant. The data are summarized in Table III and are shown graphically in Fig. 3.

TABLE III

D.S.-CARBON DISULFIDE ADDITION DATA

Run Number	CS_2, ml.	g. CS_2/g. linters	D.S.[a]
107	4	0.59	0.41
101	7	1.04	0.67
108	7	1.04	0.51
111-112	7	1.04	0.67
102	10	1.48	0.72
103	14	2.07	0.77
105	14	2.07	0.77
113-115	14	2.07	0.79
109	17	2.52	0.88
106	20	2.96	1.05
118	20	2.96	1.23

[a] Determined by ion-exchange method (Appendix I).

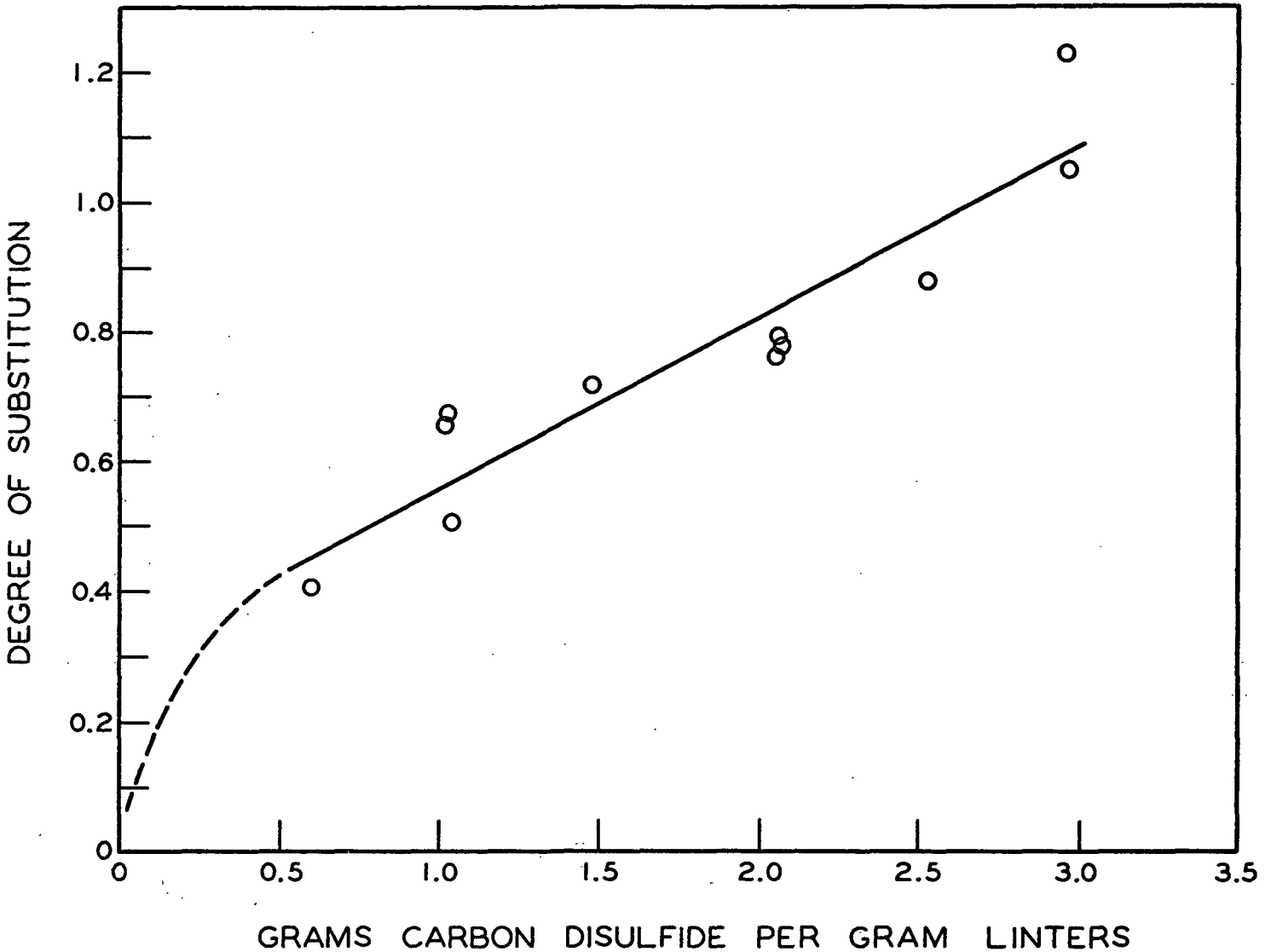

Figure 3. Emulsion Xanthation: D.S. versus Carbon Disulfide Addition

The calculated regression for the data in Table III is

$$D.S. = 0.259x + 0.302$$

where x is the grams of carbon disulfide per gram of cotton linters. The correlation coefficient (r) for the regression is 0.93.

Relationship between Viscose Composition and Carbon Disulfide Addition

The viscose composition, as determined in the laboratory, as a function of the carbon disulfide addition is given in Table IV (see also Figs. 4 and 5).

TABLE IV

VISCOSE COMPOSITION

Run Number	110-112	113-115	117	118
Cellulose, %	2.50	2.44	2.41	2.38
g. CS_2/g. linters	1.04	2.07	2.52	2.96
Total sulfur (as CS_2), %	2.67	4.51	6.24	6.58
Xanthate sulfur (as CS_2), %	0.79	0.90	0.84	1.38
By-product sulfur (as CS_2), %	1.88	3.61	5.40	5.20
Total alkali (as NaOH), %	13.84	13.61	13.48	13.66
Free NaOH (as NaOH), %	11.19	9.32	8.00	7.40
Na_2CO_3 (as NaOH), %	2.65	4.29	5.48	6.25

In the emulsion xanthation preparation of viscose, quite large excesses of carbon disulfide are employed (approximately five times that required to yield a viscose of comparable D.S. by commercial methods). Approximately 20 to 30% of the carbon disulfide was consumed in the formation of the xanthate. The remaining 70-80% existed as free carbon disulfide and sulfur by-products. Considerably greater amounts of sulfur by-products

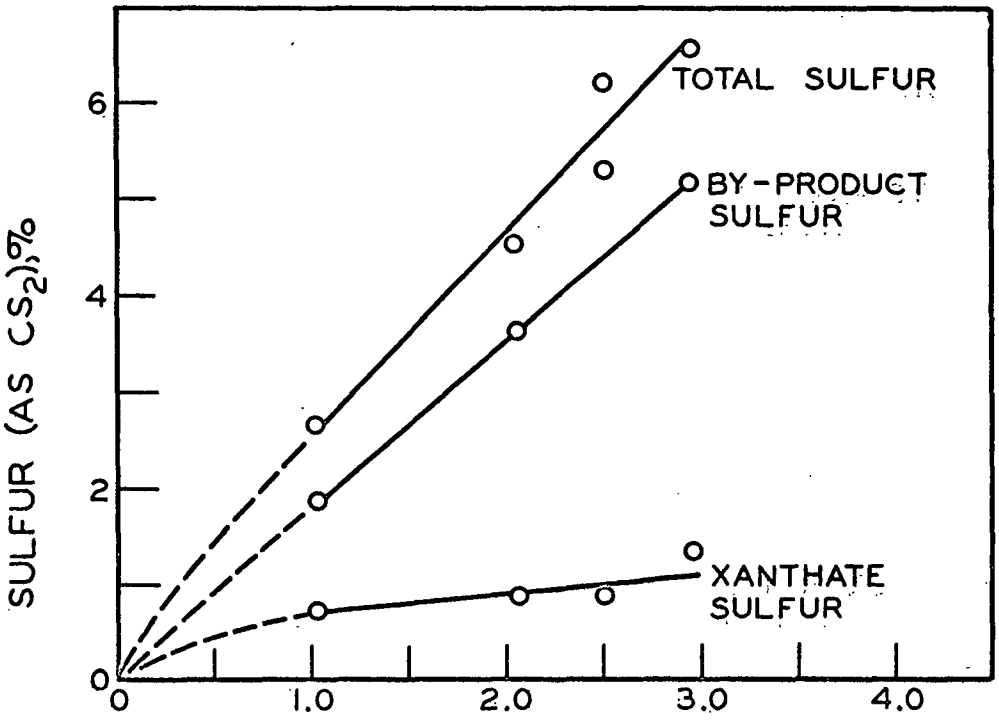

Figure 4. Emulsion Xanthation: Sulfur Distribution

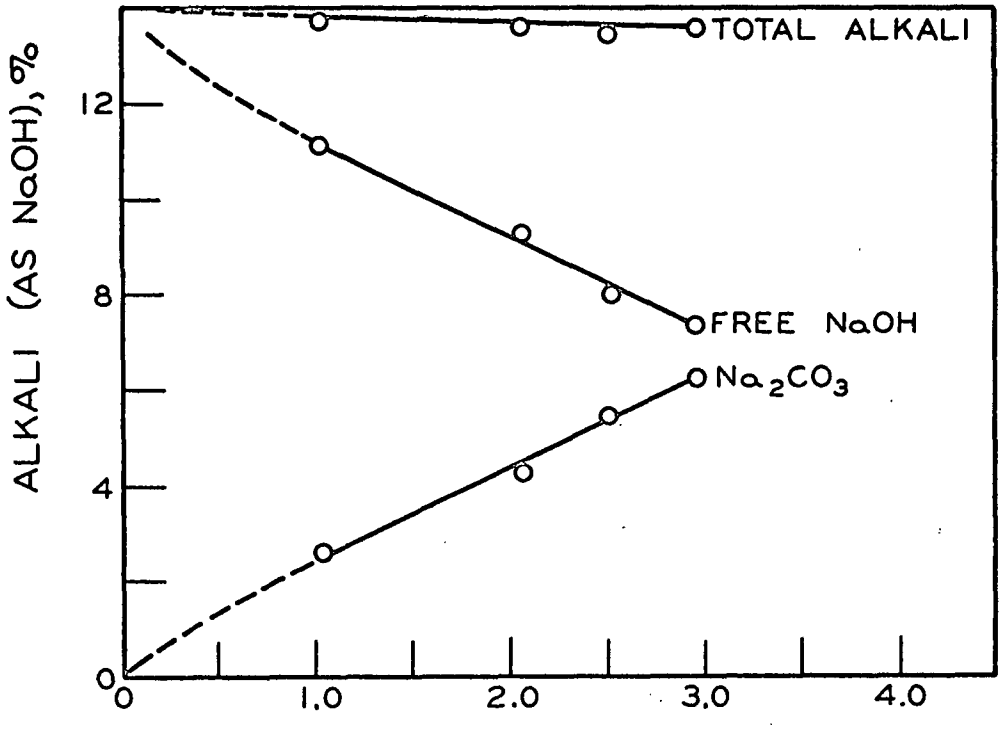

Figure 5. Emulsion Xanthation: Alkali Distribution

would be expected in viscose prepared by the emulsion xanthation technique (Fig. 3). The principal by-products would be expected to be sodium trithiocarbonate and sodium carbonate.

The total titratable alkali would include the alkali combined with the xanthate, free sodium hydroxide, sodium trithiocarbonate, and sodium carbonate.[a] This value was independent of the amount of carbon disulfide added, which was as expected (Fig. 4). The free alkali represents the titratable alkali remaining following precipitation of the carbonate as barium carbonate. This value decreased with increased carbon disulfide addition due to the increased amount of sodium carbonate in the viscose.

Relationship between D.S. and Xanthation Time

Viscose was prepared by the emulsion technique using a CS_2:cellulose ratio of 1.48. Samples, removed at 1, 2, 3, 4, and 6-hour intervals, were converted to the DAX derivative. D.S. determinations on the samples provided the data shown in Table V and Fig. 6.

Scherer and Miller (66) measured the rate of xanthation of alkali cellulose at temperatures of 25, 29.5, and 35°C. using an excess of carbon disulfide (1.52 grams carbon disulfide per gram cellulose). For comparative purposes this data was extrapolated to 20°C. These extrapolated points are shown as triangles in Fig. 6. A mathematical treatment of the data by Scherer and Miller (66) revealed that the reaction was first order. A similar treatment of the data at 20°C. for the emulsion xanthation

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[a] $2\text{Rcell-OCS}_2\text{Na} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{Rcell-OH} + \text{Na}_2\text{SO}_4 + 2\text{CS}_2$
$2\text{NaOH} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
$\text{Na}_2\text{CS}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} + \text{CS}_2$
$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$

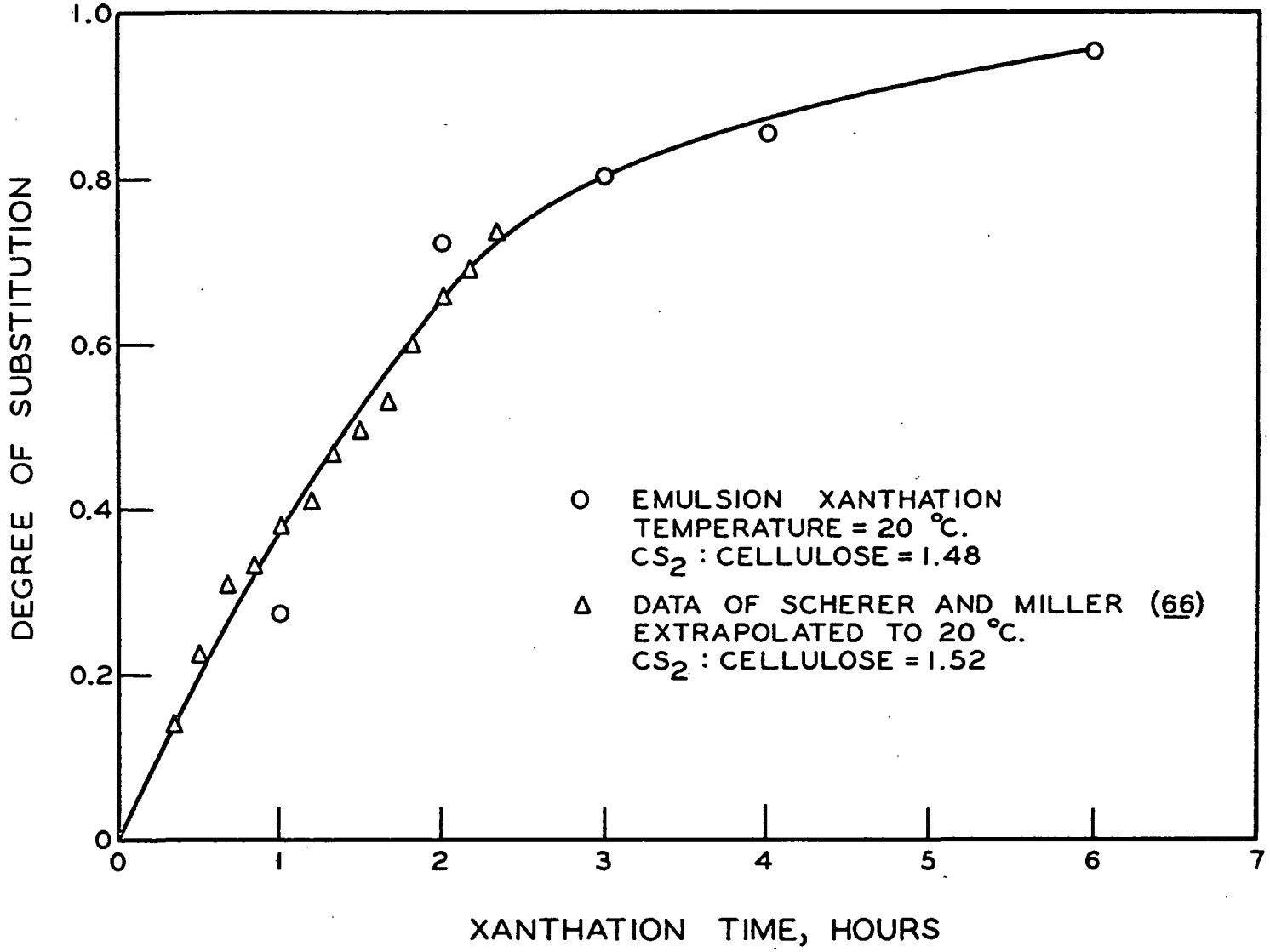

Figure 6. Emulsion Xanthation: D.S. Versus Xanthation Time

system indicated that such a conclusion was questionable (i.e., the calculated velocity constant was found to vary with time).

TABLE V

VARIATION OF XANTHATION TIME

Xanthation Time, hr.	Soluble Cellulose, %[a]	Soluble DAX, %[b]	Nitrogen in DAX, %	D.S.
1/2	61.7	--	--	--
1	91.3	0	1.79	0.27_3
2	100	15.4	3.39	0.72_2
3	100	100	3.56	0.79_4
4	100	100	3.69	0.85_1
6	100	100	3.90	0.95_4

[a] See Appendix I

[b] Solubility in 70% 2-chloroethanol

As shown in Fig. 7, the cellulose xanthate was in complete solution after approximately 75 minutes, corresponding to a D.S. of 0.44. This was in good agreement with previously reported values (66, 67). This corresponds to slightly less than one xanthate group per two glucose units. Scherer and Miller (66) have reported the required xanthation times to achieve complete solubility at 35, 29.5, and 25°C. These values were 30, 40, and 50-60 minutes, respectively.

Figure 7 also indicates the solubility of the corresponding DAX derivative prepared at various intervals in 2-chloroethanol. Previous experience had indicated that the two-hour DAX sample should be completely soluble, contrary to the results indicated in Fig. 7. D.S. determinations

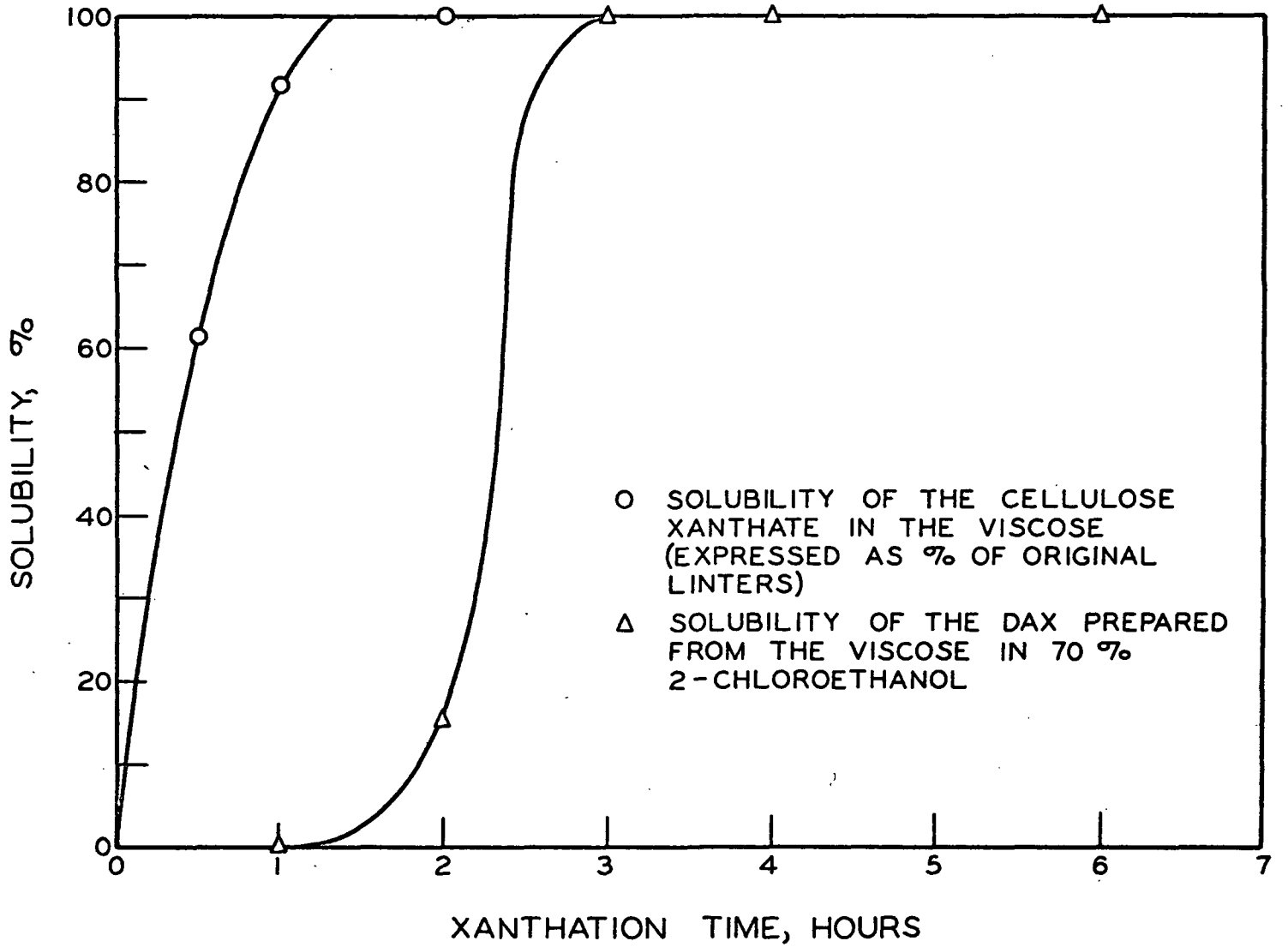

Figure 7. Emulsion Xanthation: Cellulose and DAX Solubility Versus Xanthation Time

on both the soluble and insoluble portions of the two-hour sample yielded identical values of 0.72, indicating that the relative insolubility should not be attributed to nonuniformity in substitution. The important factor influencing the solubility appeared to be the physical nature of the derivative and not the D.S. A similar conclusion has been reported by Treiber, et al. (37).

DETERMINATION OF THE VISCOSITY CONSTANT (k_m)

It is well established for other cellulose derivatives that the viscosity constant (k_m) in the modified Staudinger equation, $[\eta] = k_m D.P.$, is a function of the solvent and the D.S. of the cellulose derivative. To enable direct calculation of the D.P. of the DAX fractions from the intrinsic viscosity measurements, it was necessary to establish the relationship between k_m and D.S.

Materials

Seven fractions of the DAX derivative were chosen, covering the D.S. range 0.4-1.2.

Viscosity Data

The viscosity data for these fractions in 90% dimethyl sulfoxide are shown in Fig. 20. The corresponding intrinsic viscosities are shown in Table VI. Viscosity measurements were not obtained for the fractions in 100% dimethyl sulfoxide due to the hygroscopic nature of pure dimethyl sulfoxide.

TABLE VI

SUMMARIZED LIGHT-SCATTERING - VISCOSITY RESULTS

Sample[a]	1	2	3	4	5	6	7
D.S.	0.40	0.49	0.60	0.80	0.92	1.00	1.22
Monomer molecular weight[b]	238	255	275	313	336	351	393
$\underline{M}_w \times 10^{-5}$[c]	1.12	1.29	3.16	2.45	4.01	3.40	4.46
$D.P._w$	473	506	1150	781	1190	969	1130
$[\eta]_{90DMSO}$, dl./g.[d]	1.79	2.31	4.40	2.44	2.67	1.89	2.04
$k_{\underline{m}} \times 10^{4}$[e]	37.9	45.6	38.0	31.6	22.5	19.6	18.0

[a] For sample designation see Table XIV.

[b] Monomer molecular weight = 162.1 + 189.3 D.S.

[c] Weight average molecular weight (corrected for dissymmetry and depolarization).

[d] Intrinsic viscosity in 90% dimethyl sulfoxide.

[e] $k_{\underline{m}} = [\eta]/D.P.$

Turbidity Data

The weight average molecular weights were determined by light scattering. Further discussion of this data is included in the second portion of this thesis. The necessary corrections for dissymmetry of scattering, depolarization, fluorescence, and selective absorption have been considered.

Relationship between $k_{\underline{m}}$ and D.S.

Figure 8 shows the variation of $k_{\underline{m}}$ with D.S. for the D.S. range 0.4-1.2. Statistically, the points are satisfactorily represented by the following linear regression:

$$k_{\underline{m}} = [5.63 - 3.35 D.S.] \times 10^{-3}$$

The correlation coefficient ($\underline{r}$) is -0.93.

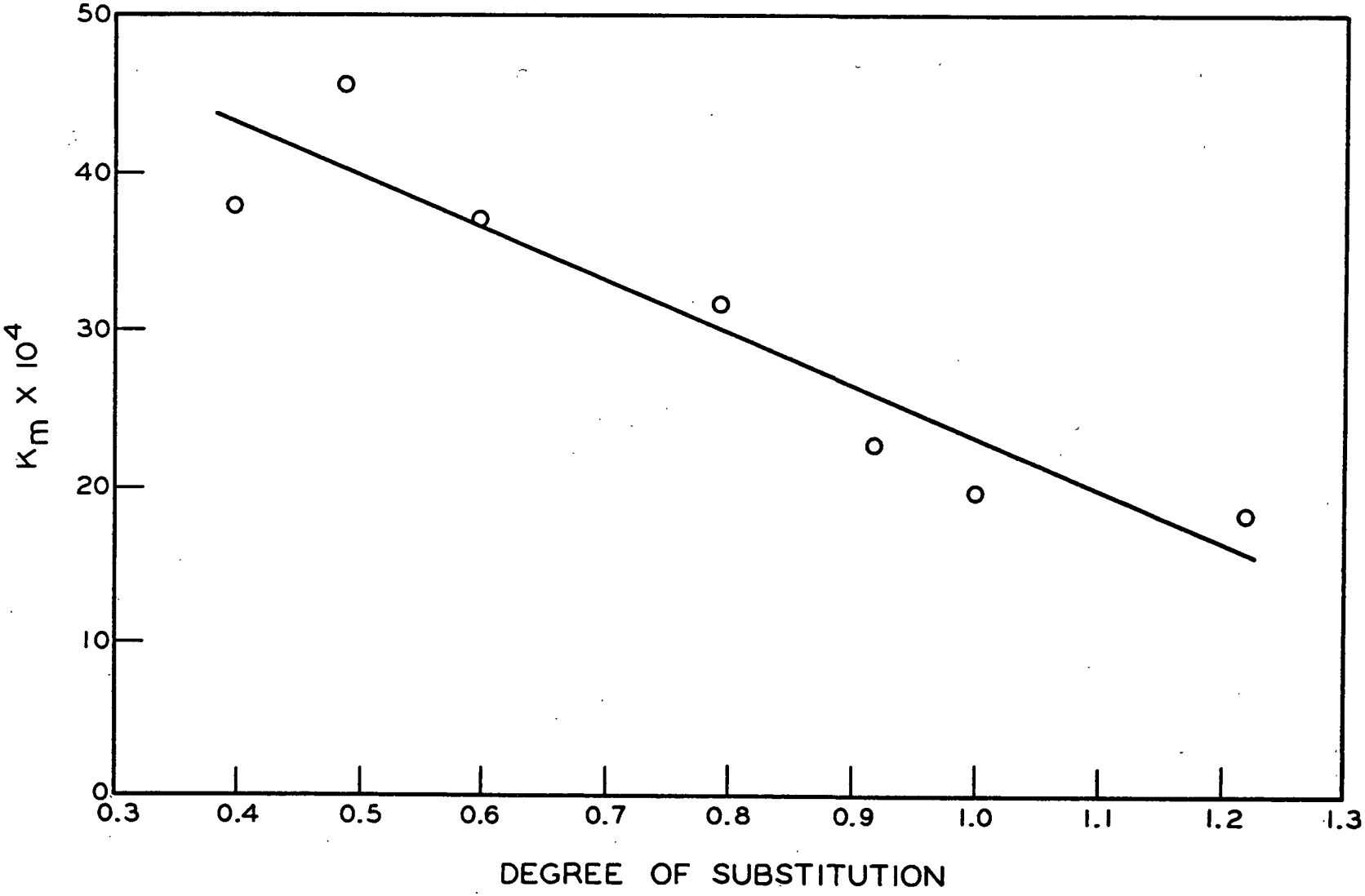

Figure 8. The Viscosity Constant (k_m) as a Function of D.S. for the DAX Derivative in 90DMSO

The Staudinger equation for the DAX derivative in 90% dimethyl sulfoxide at a temperature of 25°C. may be written in the following form:

$$[\eta]_{90DMSO} = [5.63 - 3.35D.S.] \times 10^{-3} D.P._{\underline{w}}$$

Schurz and Armbrüster (6) have recently published the following form of this relationship for the DAX derivative in 100% dimethyl sulfoxide[a]:

$$[\eta]_{100DMSO} = [12.2 - 7.83D.S.] \times 10^{-3} D.P._{\underline{w}}$$

Both of these relationships may be reduced to a similar form by extracting the slope term of the $k_{\underline{m}}$ versus D.S. plot as follows:

$$[\eta]_{90DMSO} = 3.35[1.68 - D.S.] \times 10^{-3} D.P._{\underline{w}}$$

$$[\eta]_{100DMSO} = 7.83[1.56 - D.S.] \times 10^{-3} D.P._{\underline{w}}$$

The relationships, therefore, are quite in agreement, assuming that the ratio $[\eta]_{90DMSO}/[\eta]_{100DMSO}$ is equal to 0.43.

EFFECT OF CARBON DISULFIDE ADDITION ON THE UNIFORMITY OF SUBSTITUTION

Fractionation Samples

The DAX derivatives employed in the subsequent fractionations are listed in Table VII.

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[a] The work of Schurz and Armbrüster (6) was published while this thesis was in progress. The authors indicated that the data from which the given form of the Staudinger equation was derived was to be published in the near future.

TABLE VII

FRACTIONATION SAMPLES

Sample	Xanthation Ratio, g. CS_2/g. linters	Viscose D.S.[a]	Nitrogen in DAX, %	DAX D.S.[b]
A	1.04	--	3.02	0.59
B	1.48	--	3.69	0.95
C	2.96	1.11	4.03	1.02
D	2.96	1.23	4.22	1.16
E	2.52	0.744	--	--

[a] D.S. determined directly on the viscose by the ion-exchange method (Appendix I).

[b] D.S. calculated from the nitrogen content of the DAX derivative.

Fractionation Data

DAX A-E

Common methods of fractionation, i.e., precipitation and solution, lead to a distribution of molecular species between two phases. The respective concentrations in the two phases are dependent upon the difference in potential energy of the substance in the two phases (68). Wadano (69) has related this potential energy difference to D.P., D.S., and liquid concentration.

Up to the time this thesis work was undertaken, it had not adequately been established whether D.P. or D.S. was the predominating influence on the fractionation of the DAX derivative from a 2-chloroethanol--water system. It was necessary, therefore, to determine whether such a fractionation technique would successfully show up differences in D.S. in the derivative.

Equal amounts of DAX A (D.S. = 0.59) and DAX E (D.S. = 0.74) were mixed together to give a sample of average D.S. equal to 0.66. The D.P. distributions of the two samples were assumed to be quite similar. This has been substantiated by subsequent fractionation data. If fractionation occurs strictly according to D.P., all of the fractions will have D.S. values between 0.59 and 0.74. If fractionation occurs according to D.S., fractions having D.S. values both higher and lower than this range will be expected.

A total of six fractions were obtained by fractional precipitation from a 70% 2-chloroethanol solution. The total recovery from the fractionation was 86%. The fractionation data are summarized in Table VIII, and the viscosity data are shown in Appendix II. The weighted average D.S. from the fractionation was 0.66, indicating negligible loss of acetamide groups. The significant decrease in D.S. with succeeding fractionation is shown in Fig. 9.

The viscosity values shown in Table VIII appear somewhat surprising in that the values for Fractions IV and V were considerably higher than that for Fraction I. Fractions I-III accounted for 50% of the DAX recovered by the fractionation and had a weighted average D.S. of 0.75, while Fractions IV-VI accounted for the remaining 50% and had a weighted average D.S. of 0.59. Evidently DAX A and DAX E have been separated successfully by this fractionation technique. The evidence strongly indicated that in the case of large differences in substitution, D.S. is the predominating influence on the course of the fractionation. This is contrary to the recently published assumption that D.P. is the controlling factor (6, 40).

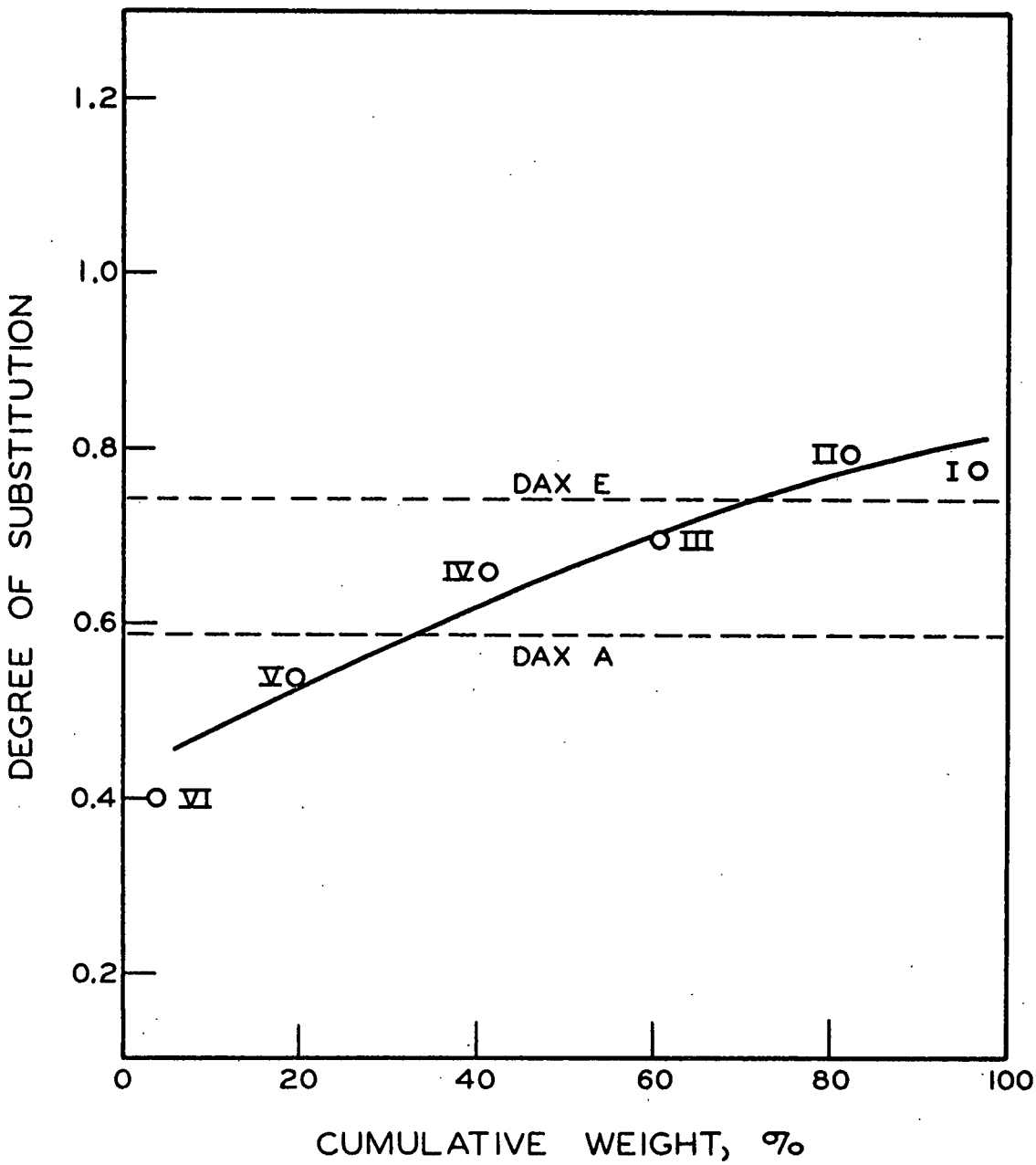

Figure 9. D.S. Versus Cumulative Weight Per Cent for DAX A-E

TABLE VIII

FRACTIONATION DATA - DAX A-E (AV. D.S. = 0.66)

Fraction	Wt., %	Cumulative Wt., %	Nitrogen, %	D.S.	$[\eta]_{90DMSO}$, dl./g.
I	6.2	100.0	3.51	0.77	2.72
II	22.1	93.8	3.56	0.80	2.44
III	21.7	71.7	3.32	0.70	1.96
IV	17.8	50.0	3.21	0.66	3.65
V	25.9	32.2	2.85	0.54	2.98
VI	6.3	6.3	2.35	0.40	1.79
Weighted average (Fractions I-VI)				0.66	2.67
Weighted average (Fractions I-III)				0.75	2.27
Weighted average (Fractions IV-VI)				0.56	3.07

DAX A

The D.S. of the unfractionated derivative was 0.59, compared with an average value of 0.55 from the fractionation. A total of thirteen fractions were isolated by fractionation from a 70% 2-chloroethanol solution. Fraction XIII was obtained by adding a large excess of water and cooling for several days. The total recovery was 99%.

The viscosity, D.P., and molecular weight data are summarized in Table IX. The intrinsic viscosities were determined by the extrapolation of log $\eta_{sp}/\underline{c}$ to zero concentration (Appendix II).

Plotting the cumulative D.S. in per cent (Σ D.S. %) versus the cumulative weight per cent in the manner of Timell and Purves (1), gives an indication of the homogeneity of substitution. The diagonal represents a derivative of completely homogeneous composition. Such

TABLE IX

FRACTIONATION DATA - DAX A (D.S. = 0.59)

Fraction	Wt., %	Cumulative Wt., %	Nitrogen, %	D.S.	D.S., %	Cumulative D.S., %	$[\eta]_{90DMSO}$, dl./g.	D.P.$_w$	$M_w \times 10^{-5}$
I	11.0	100.0	2.99	0.58	11.7	100.0	6.26	1700	4.63
II	14.6	89.0	2.96	0.57	15.2	88.3	5.39	1450	3.91
III	12.6	74.4	2.92	0.56	12.8	73.1	4.75	1260	3.38
IV	9.5	61.8	3.04	0.60	10.4	60.3	4.40	1210	3.33
V	5.3	52.3	2.95	0.57	5.6	49.9	3.93	1050	2.84
VI	6.2	47.0	2.85	0.54	6.1	44.3	3.64	948	2.54
VII	8.7	40.8	2.76	0.51	8.0	38.2	3.45	881	2.27
VIII	5.2	32.1	2.75	0.51	4.8	30.1	2.91	741	1.91
IX	3.7	26.9	2.70	0.49	3.4	25.3	2.50	628	1.60
X	6.5	23.2	2.69	0.49	5.9	21.9	2.38	596	1.52
XI	6.7	16.7	2.66	0.48	5.8	16.0	1.96	488	1.23
XII	5.9	10.0	2.92	0.56	6.0	10.2	1.58	420	1.13
XIII	4.1	4.1	2.93	0.56	4.2	4.2	1.18	314	0.84
Weighted average				0.55			4.00	1036	3.01

a plot for DAX A is shown in Fig. 10. The apparent deviation from the diagonal is an indication that the longer chain molecules are more highly substituted.

DAX B

The D.S. of the unfractionated derivative was 0.95, compared with an average value of 0.94 from the fractionation. Five fractions were separated by fractionation from 70% 2-chloroethanol. Fraction I (71.3%) was refractionated into three fractions (I-1, I-2, and I-3). The total recovery, therefore, was rather low (84%).

The fractionation data are summarized in Table X. The viscosity data are shown in Appendix II. The substitution-distribution plot is shown in Fig. 11.

DAX C

The D.S. of the unfractionated DAX was 1.02, compared with an average value of 0.97 from the fractionation. A total of sixteen fractions were isolated and combined to give a total of ten fractions. The total recovery was 87%.

The summarized fractionation data are shown in Table XI; the viscosity data, in Appendix II; and the substitution-distribution plot in Fig. 12.

DAX D

The D.S. of the unfractionated derivative was 1.23, compared with an average value of 1.21 from the fractionation. A total of sixteen fractions were isolated, accounting for 91% of the starting material.

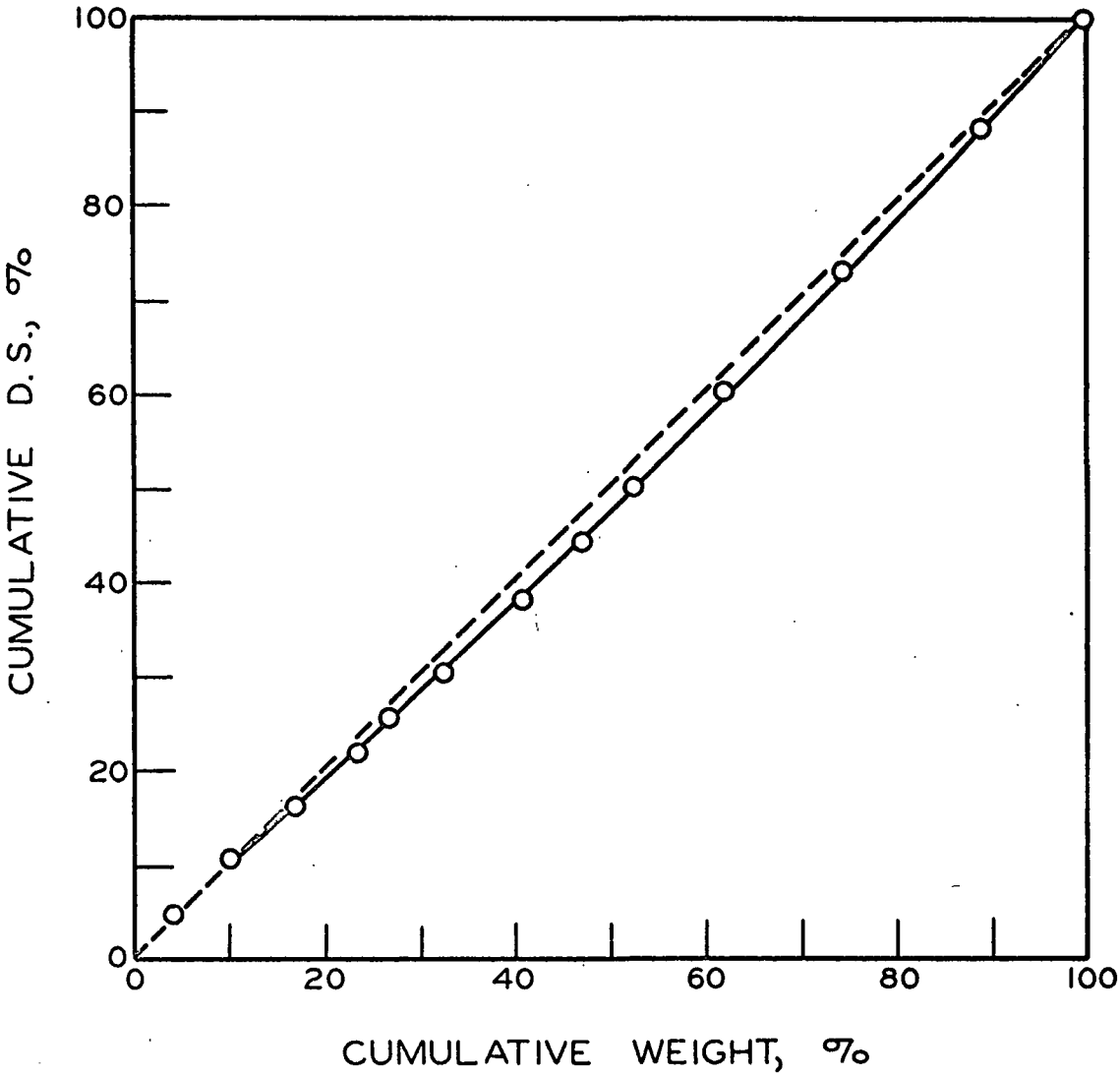

Figure 10. Substitution-Distribution Curve for DAX A

TABLE X

FRACTIONATION DATA - DAX B (D.S. = 0.95)

Fraction	Wt., %	Cumulative Wt., %	Nitrogen, %	D.S.	D.S., %	Cumulative D.S., %	$[\eta]_{90DMSO}$, dl./g.	$D.P._w$	$M_w \times 10^{-5}$
I-1	9.0	100.0	3.93	0.97	9.4	100.0	4.66	1950	6.75
I-2	49.5	91.0	3.90	0.95	50.3	90.6	3.13	1280	4.39
II	7.0	41.5	3.87	0.94	7.0	40.3	2.44	980	3.34
I-3	12.8	34.5	3.76	0.89	12.1	33.3	1.65	618	2.04
III	9.7	21.7	3.90	0.95	9.9	21.2	1.29	529	1.81
IV	7.0	12.0	3.73	0.87	6.5	11.3	1.29	475	1.55
V	5.0	5.0	3.81	0.91	4.8	4.8	0.71	274	0.92
Weighted average				0.94			2.60	1065	3.61

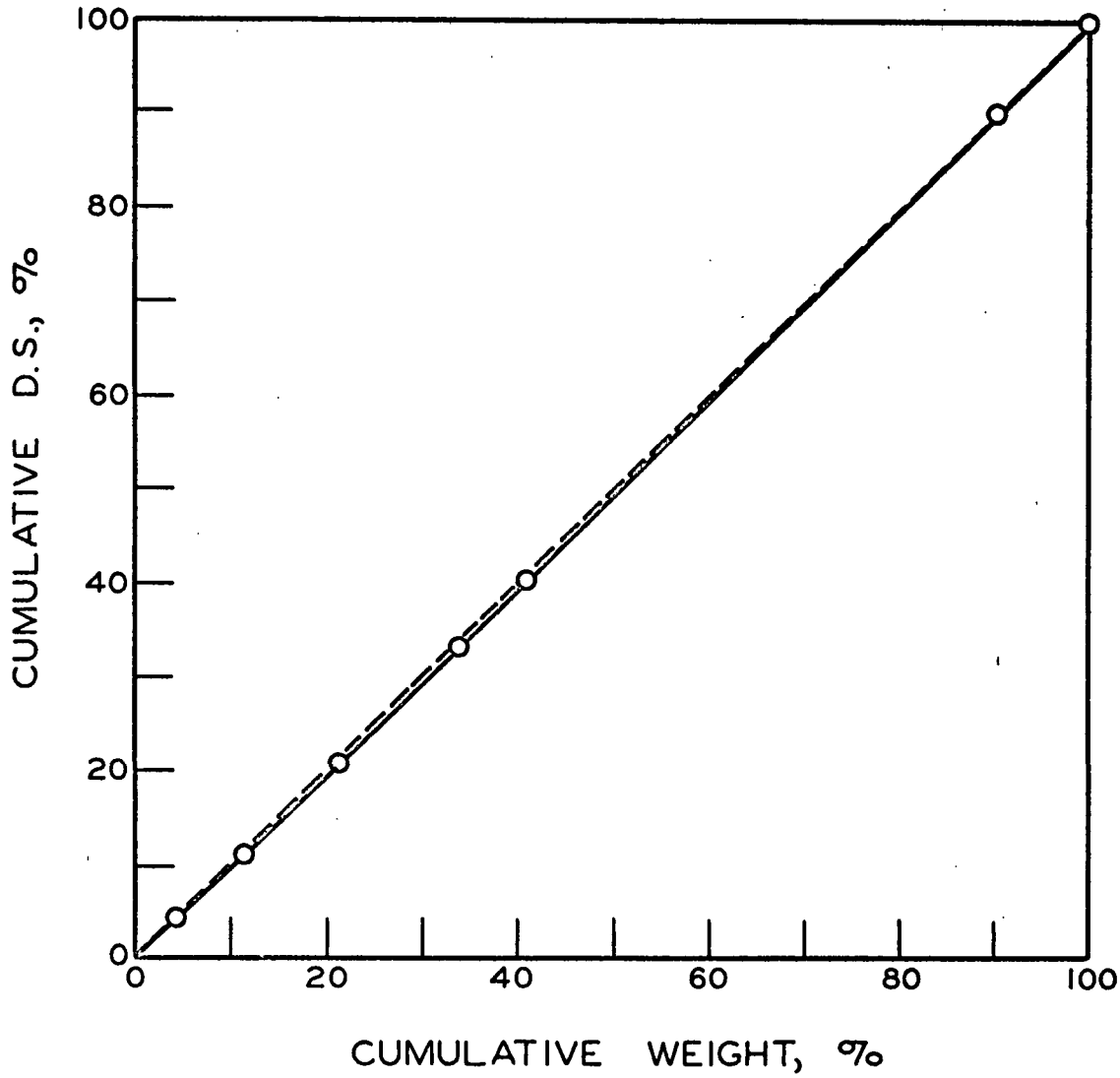

Figure 11. Substitution-Distribution Curve for DAX B

TABLE XI

FRACTIONATION DATA - DAX C (D.S. = 1.02)

Fraction	Wt., %	Cumulative Wt., %	Nitrogen, %	D.S.	D.S., %	Cumulative D.S., %	$[\eta]_{90DMSO}$, dl./g.	$D.P._w$	$M_w \times 10^{-5}$
I	7.3	100.0	3.97	0.99	7.4	100.0	3.17	1370	4.95
II	5.0	92.7	3.98	1.00	5.2	92.6	3.21	1405	4.94
III	21.4	87.7	3.98	1.00	22.1	87.4	3.11	1365	4.80
IV	4.7	66.3	4.00	1.01	4.9	65.3	3.18	1415	5.00
V	16.1	61.6	3.88	0.95	15.6	60.4	2.91	1170	3.98
VI	11.8	45.5	3.83	0.92	11.3	44.8	2.67	1055	3.55
VII	11.2	33.7	3.92	0.96	11.2	33.5	2.29	947	3.25
VIII	5.5	22.5	3.98	1.00	5.7	22.3	1.89	830	2.91
IX	6.5	17.0	3.89	0.95	6.4	16.6	1.53	624	2.13
X	10.5	10.5	3.90	0.95	10.2	10.2	1.09	445	1.52
Weighted average				0.97			2.56	1083	3.75

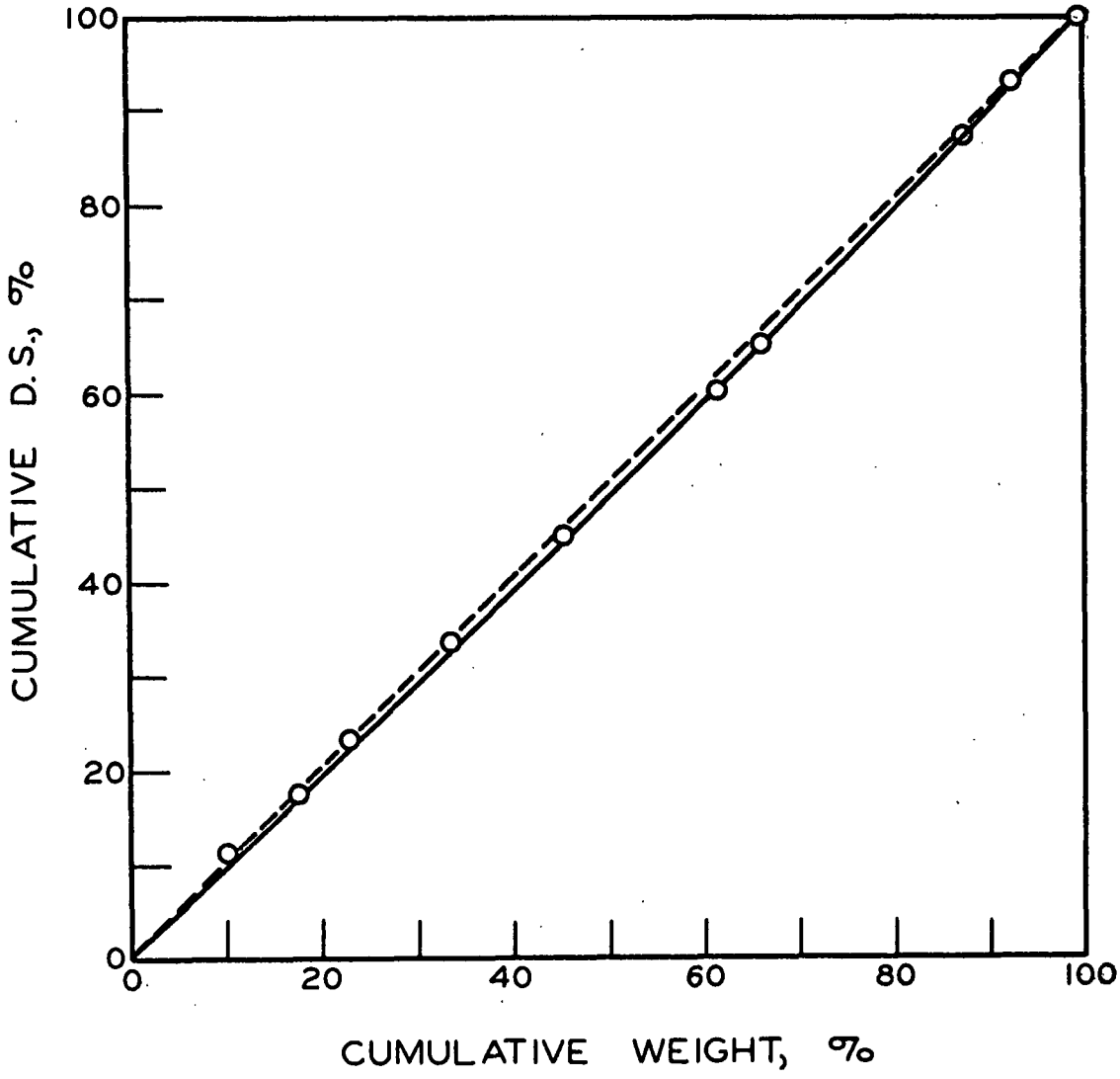

Figure 12. Substitution-Distribution Curve for DAX C

Since the intrinsic viscosities for the fractions were determined originally in 70% 2-chloroethanol, viscosities for only five fractions were determined in 90% dimethyl sulfoxide (Appendix II). The plot of $[\eta]_{90DMSO}$ versus $[\eta]_{70ECH}$ shown in Fig. 13 enabled conversion of the viscosities of the remaining fractions to the corresponding values in 90% dimethyl sulfoxide.

The fractionation data are summarized in Table XII. As indicated in Fig. 14, substitution appears to be quite uniform at this D.S. level.

D.P. and D.P. Distribution of the DAX Derivatives

The weighted average $D.P._w$ obtained from the fractionation data were as follows: DAX A, 1035; DAX B, 1065; DAX C 1083; and DAX D, 1484. With the exception of DAX D these values correspond well with the value obtained for the original linters (1135). This result is in agreement with the conclusion of Jayme, et al. (54, 55) that degradation during emulsion xanthation is negligible. The high value for DAX D is attributed to the possible loss of low D.P. material during the preparation of the derivative and/or the possible error introduced in the viscosity conversion.

The integral weight distributions for the DAX derivatives are shown in Fig. 15, along with the distribution for the original linters. The distributions shown for DAX A and DAX B corresponded closely to that of the linters. The distributions for DAX C and DAX D indicated the possible loss of low D.P. material. As reflected by these data, the differential curve shown in Fig. 1 for the linters may be two-peaked with maxima at 500 and 1000. It appeared that some degradation during the viscose preparation occurred in the high D.P. range.

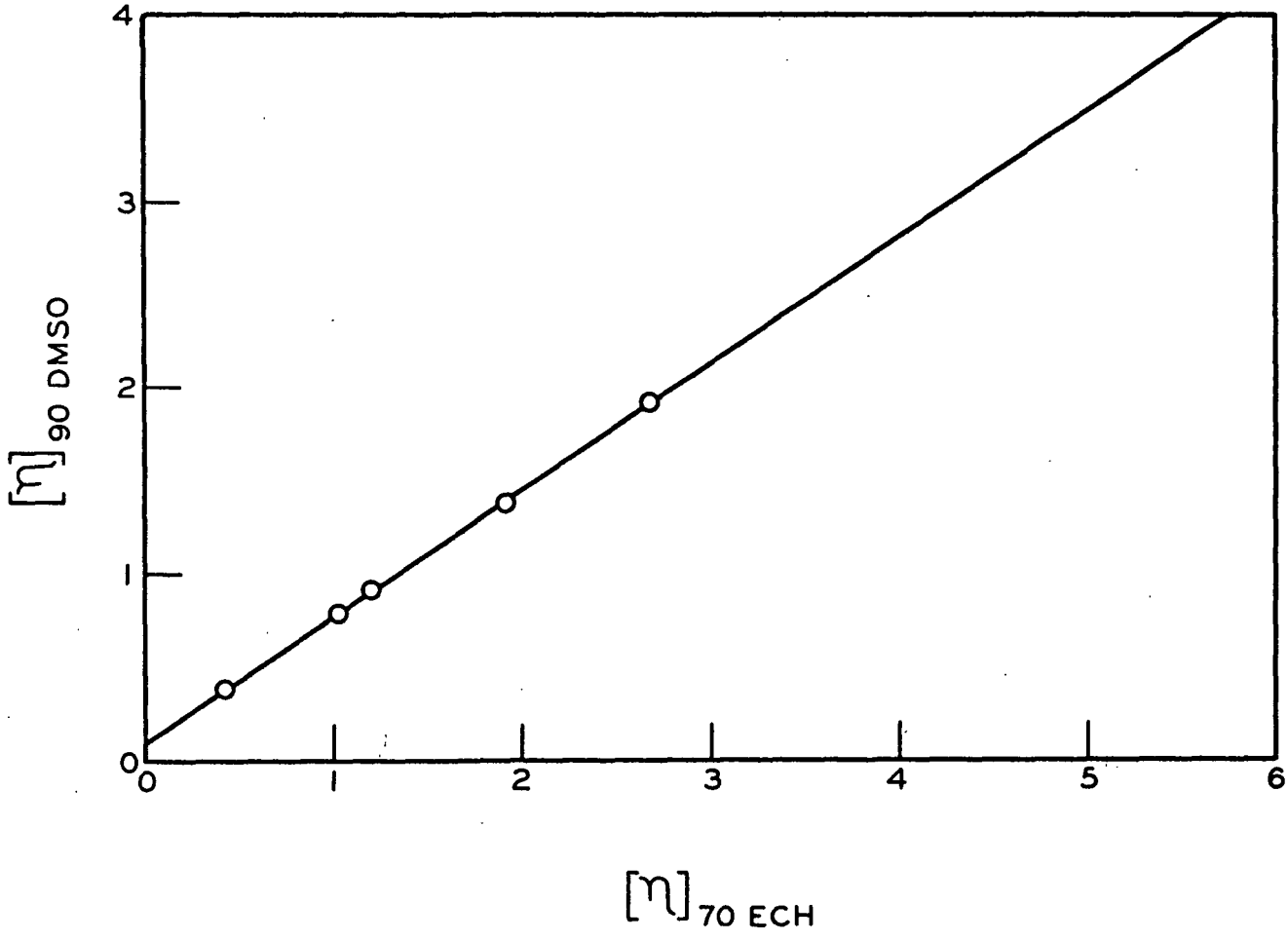

Figure 13. Intrinsic Viscosity Conversion Plot for DAX D

TABLE XII

FRACTIONATION DATA - DAX D (D.S.[a] = 1.23)

Fraction	Wt., %	Cumulative Wt., %	Nitrogen, %	D.S.	D.S., %	Cumulative D.S., %	$[\eta]_{7OECH}$, dl./g.	$[\eta]_{90DMSO}$, dl./g.	$D.P._w$	$M_w \times 10^{-5}$
I	1.8	100.0	4.10	1.06	1.6	100.0	5.30	3.64	1925	6.99
II	6.4	98.2	4.31	1.19	6.3	98.4	5.12	3.52	2130	8.27
III	42.4	91.8	4.34	1.22	42.9	92.1	4.45	3.06	1960	7.72
IV	5.8	49.4	4.32	1.20	5.8	49.2	3.83	2.64	1630	6.35
V	5.4	43.6	4.34	1.22	5.9	43.4	3.32	2.30	1470	5.79
VI	6.8	38.2	4.27	1.17	6.6	37.5	2.69	1.90	1105	4.24
VII	5.5	31.4	4.33	1.21	5.5	30.9	2.39	1.68	1055	4.12
VIII	4.0	25.9	4.35	1.23	4.1	25.4	2.34	1.65	1085	4.28
IX	2.3	21.9	4.34	1.22	2.3	21.3	2.17	1.53	982	3.87
X	2.8	19.6	4.35	1.23	2.9	19.0	1.91	1.35	895	3.53
XI	5.2	16.8	4.28	1.18	5.1	16.1	1.79	1.28	758	2.93
XII	1.5	11.6	4.34	1.22	1.5	11.0	1.20	0.91	583	2.30
XIII	3.7	10.1	4.20	1.13	3.5	9.5	1.10	0.83	448	1.69
XIV	2.2	6.4	4.28	1.18	2.2	6.0	1.02	0.78	461	1.78
XV	2.1	4.2	4.12	1.08	1.9	3.8	0.75	0.59	292	1.07
XVI	2.1	2.1	4.28	1.18	1.9	1.9	0.43	0.38	222	0.86
Weighted average				1.21			3.42	2.38	1484	5.78

[a] D.S. value determined upon the original viscose

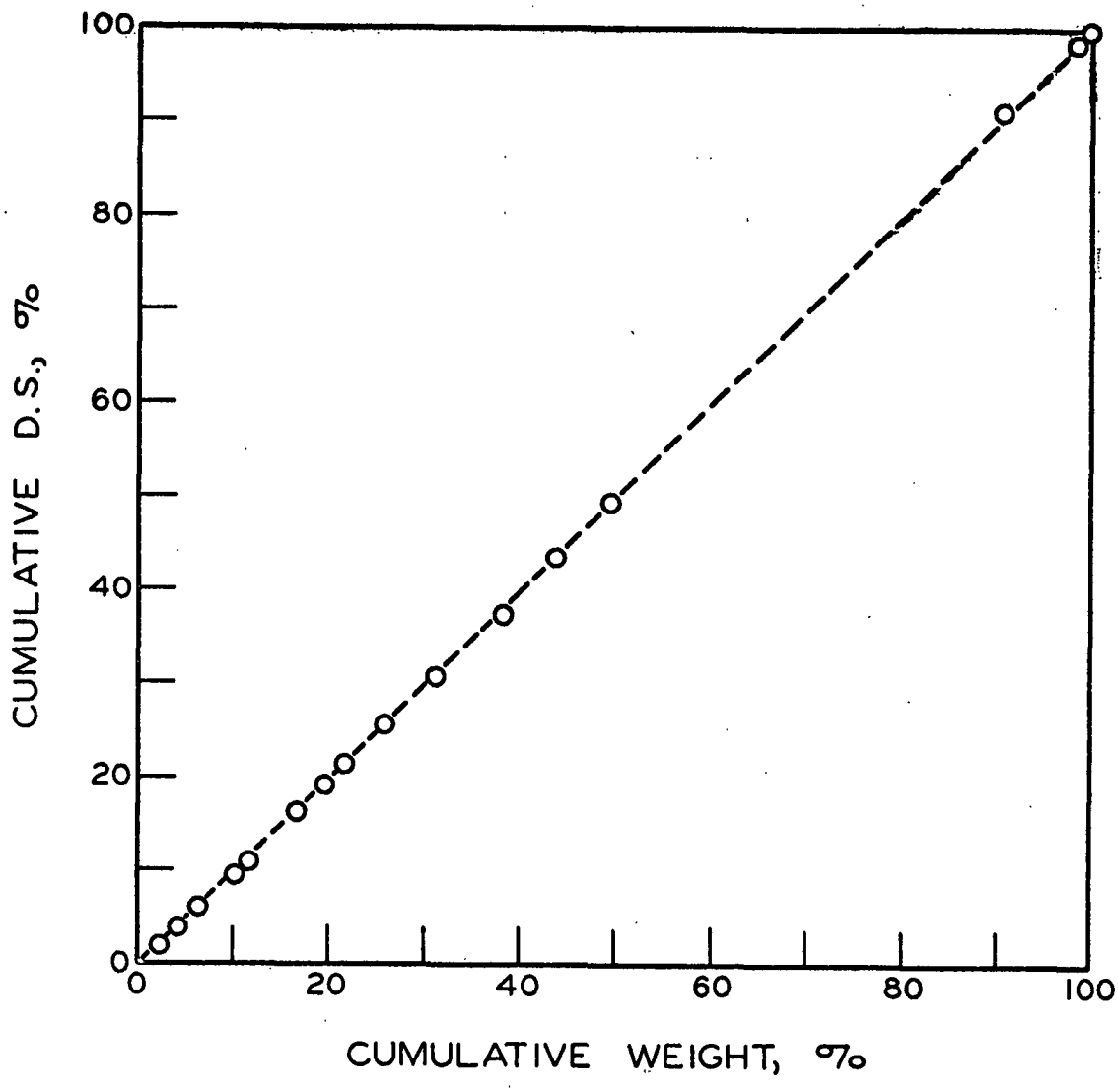

Figure 14. Substitution-Distribution Curve for DAX D

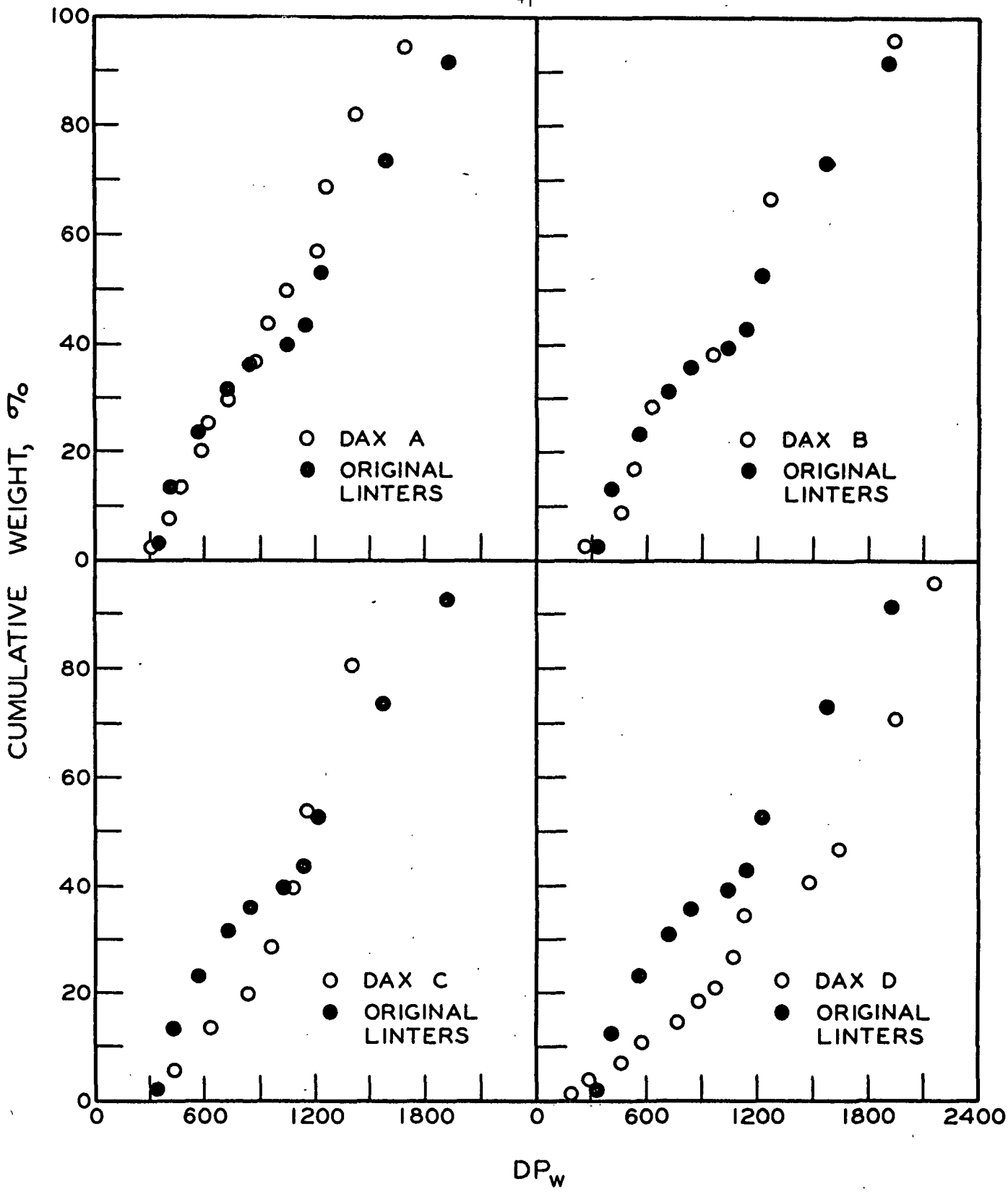

Figure 15. Integral Weight Distributions: Original Linters, DAX A, DAX B, DAX C, DAX D

Relationship between D.S. and D.P.

The D.P.-D.S. data for the fractionated derivatives A, B, C, and D are shown in Tables IX-XII. The substitution-distribution curves (Figs. 10, 11, 12, 14) indicate that the longer cellulose chains have a higher D.S. than the shorter chains. This is clearly apparent in the D.S.-D.P. plots shown in Fig. 16.

Assuming linearity, the calculated "least square" regressions are as follows:

Viscose A (D.S. = 0.55[a])	$D.S. = (5.71 \times 10^{-5})D.P._w + 0.488$
Viscose B (D.S. = 0.94)	$D.S. = (4.57 \times 10^{-5})D.P._w + 0.887$
Viscose C (D.S. = 0.97)	$D.S. = (4.51 \times 10^{-5})D.P._w + 0.924$
Viscose D (D.S. = 1.21)	$D.S. = (3.37 \times 10^{-5})D.P._w + 1.157$

The calculated correlation coefficients are 0.62, 0.70, 0.53, and 0.63. The regressions for viscoses A and D are within the 5% level of significance as determined by the "F" test, while the regressions for viscoses B and C are slightly outside of the 5% level.

The generalized relationship for a given D.S. level may be written in the following form:

$$D.S. = \beta D.P._w + D.S._o$$

where β and $D.S._o$ are functions of the D.S. of the unfractionated viscose. As the viscose D.S. is increased, β approaches a value of zero indicating that substitution becomes increasingly homogeneous with respect to chain length. In the emulsion xanthation technique this would correspond to increasing the carbon disulfide in the system. Conversely, decreasing the

[a] The D.S. values listed are the average values obtained from the fractionation data.

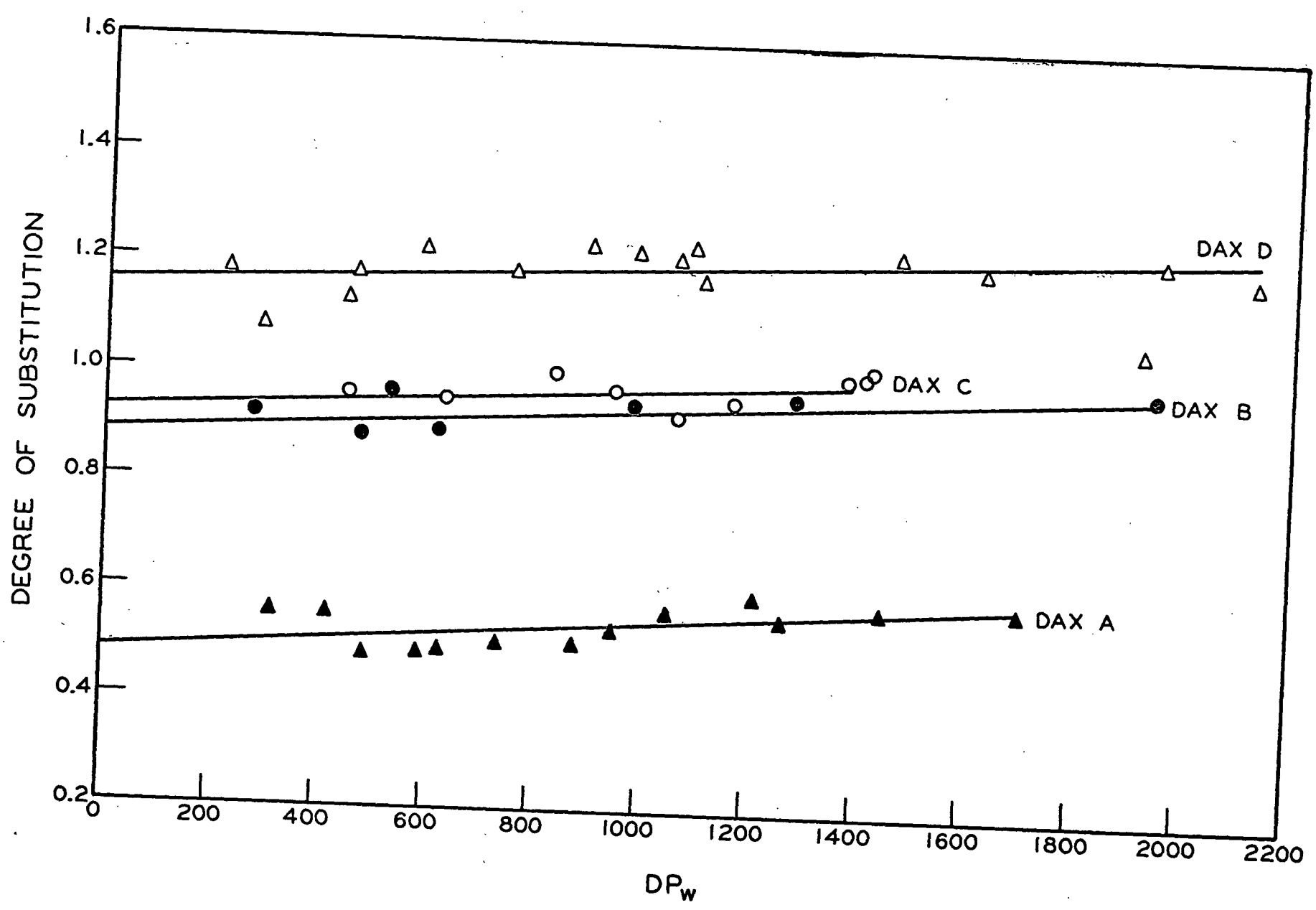

Figure 16. D.S.-D.P. Plot for Viscoses A, B, C, and D

amount of carbon disulfide increases the nonuniformity of substitution. The effect is shown in Fig. 17, where β has been plotted as a function of the average D.S. of the viscose. It appears that the relationship may be reasonably linear over the D.S. range 0.5-1.2.

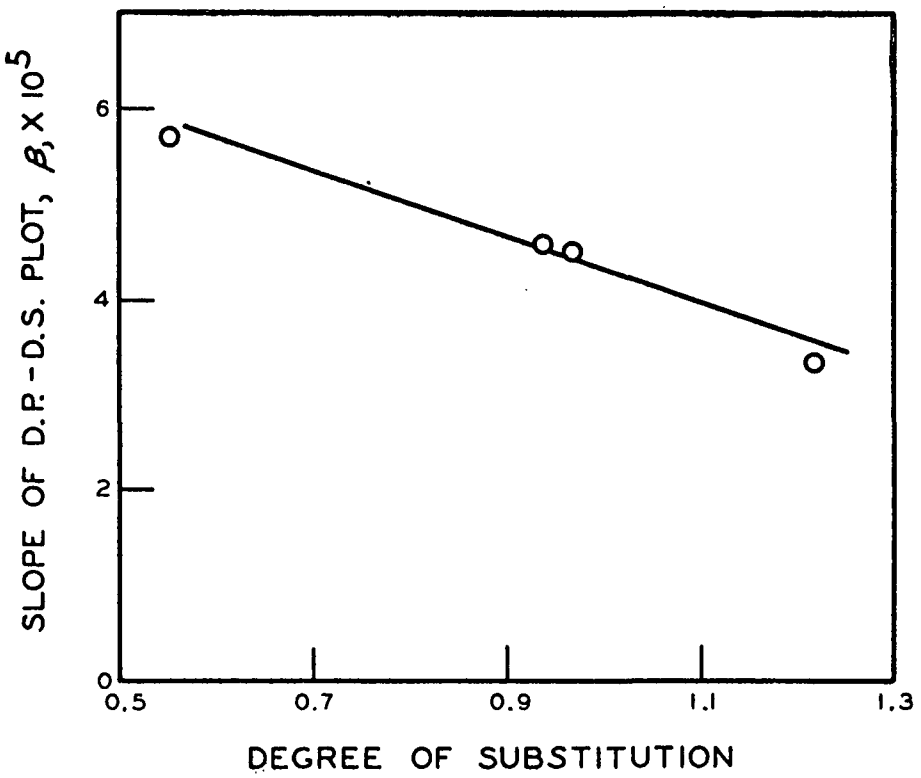

Figure 17. Nonuniformity Factor, β, as a Function of the Viscose D.S.

Yamada and Mukoyama (40) have recently published data for the fractionation of a DAX derivative with a D.S. of 0.48. A similar treatment of their data by this author (R.H.C.) led to a value of β of approximately 14.5×10^{-5}, indicating a significantly higher nonuniformity in substitution than that found in this work. This result, however, was not unexpected since the authors were concerned with viscose prepared by the addition of appreciably smaller amounts of carbon

disulfide. The data of Schurz and Armbrüster (6), on the other hand, would indicate a negative value of β for a fractionated DAX sample with a D.S. of 0.55. This cannot be reconciled with the above findings.

The emulsion xanthation system greatly contrasts commercial viscose preparation. Commercial alkali cellulose is normally xanthated in the "crumb" form with gaseous carbon disulfide. Morphology and accessibility greatly influence the rate, homogeneity, and the final degree of xanthation. In contrast, the cellulose fibers are suspended in an alkaline medium in the presence of a large excess of carbon disulfide during emulsion xanthation. Concomitant reaction of the cellulose with alkali, leading to the formation of alkali cellulose, and reaction of the alkali cellulose with the carbon disulfide occur. The total surface area available for xanthation is expected to be greater than that available in commercial xanthation. The anticipated result would be a more uniform, more rapid reaction.

It appears that the controlling factor during emulsion xanthation is the inherent solubility of the xanthated cellulose chains in the alkaline medium. Presumably the shorter, more accessible chains dissolve at a lower D.S. level than the longer chains. In effect, this infers that there is a progressive dissolution of the cellulose to the point where the cellulose is completely in solution as the xanthate. Subsequent xanthation ("after" xanthation) is retarded due to hydrolysis or saponification. Higher concentration of the carbon disulfide in the immediate vicinity of the undissolved cellulose xanthate appears quite likely, considering the nature of the system. The net result of these factors is a higher rate of xanthation for cellulose in the undissolved state than for the cellulose

already dissolved as the xanthate. As shown in Fig. 7, complete solution was obtained in somewhat over one hour for a CS_2:cellulose ratio of 1.48. The D.S. of the xanthate at this point corresponded to 0.44. In all probability, nonuniformity in substitution was a maximum at this point.

EFFECT OF XANTHATION TIME ON THE UNIFORMITY OF SUBSTITUTION

In the previous discussion it has been suggested that the uniformity of substitution with regard to chain length would decrease with a decrease in xanthation time. It had been hoped that it would be possible to fractionate a sample of the DAX derivative prepared immediately following complete solution of the cellulose xanthate. This was, however, not possible since the DAX derivative was only slightly soluble (0-3%) in 2-chloroethanol at this point (Fig. 7). Therefore, samples of the DAX derivative (B-3, B-4, and B-6) were prepared at intervals of three, four, and six hours xanthation time. The xanthation ratio (CS_2:cellulose) was 1.48. Samples DAX B-4 and DAX B-6 were prepared from the same viscose run, while DAX B-3 was prepared from a separate run under identical conditions.

The fractionation data for DAX B-3 and DAX B-4 are given in Table XIII, while that for DAX B-6 has already been presented in Table X. The viscosity data are shown in Appendix II. The yields for the fractionations were 93, 93, and 84%, respectively. The low yield for DAX B-6 was due to the refractionation of Fraction I. The weighted average $D.P._w$ values were 882, 1118, and 1065, respectively.

The D.P.-D.S. plots for these fractionations are shown in Fig. 18. The calculated "least square" regressions are as follows:

TABLE XIII

FRACTIONATION DATA - DAX B-3 (D.S. = 0.79)

Fraction	Wt., %	Cumulative Wt., %	Nitrogen, %	D.S.	D.S., %	Cumulative D.S., %	$[\eta]_{90DMSO}$, dl./g.	$D.P._w$	$M_w \times 10^{-5}$
I	23.5	100.0	3.62	0.82	24.9	100.0	3.52	1219	3.86
II	15.3	76.5	3.62	0.82	16.1	75.1	3.43	1188	3.77
III	14.7	61.2	3.41	0.73	13.9	59.0	2.62	862	2.63
IV	10.2	46.5	3.56	0.80	10.4	45.1	2.58	870	2.72
V	18.9	36.3	3.54	0.79	19.2	34.7	2.18	730	2.27
VI	7.9	17.4	3.34	0.70	7.1	15.5	1.29	393	1.16
VII	9.5	9.5	3.27	0.68	8.4	8.4	1.00	298	0.87

FRACTIONATION DATA - DAX B-4 (D.S. = 0.85)

I	24.7	100.0	3.73	0.87	25.7	100.0	4.83	1775	5.80
II	35.0	75.3	3.67	0.84	35.1	74.3	3.42	1210	3.88
III	14.9	40.3	3.65	0.84	14.9	39.2	2.51	887	2.84
IV	16.2	25.4	3.57	0.80	15.4	24.3	1.78	600	1.88
V	9.2	9.2	3.60	0.81	8.9	8.9	0.78	268	0.85
Weighted average									
DAX B-3				0.78			2.61	882	2.74
DAX B-4				0.84			3.12	1118	3.61

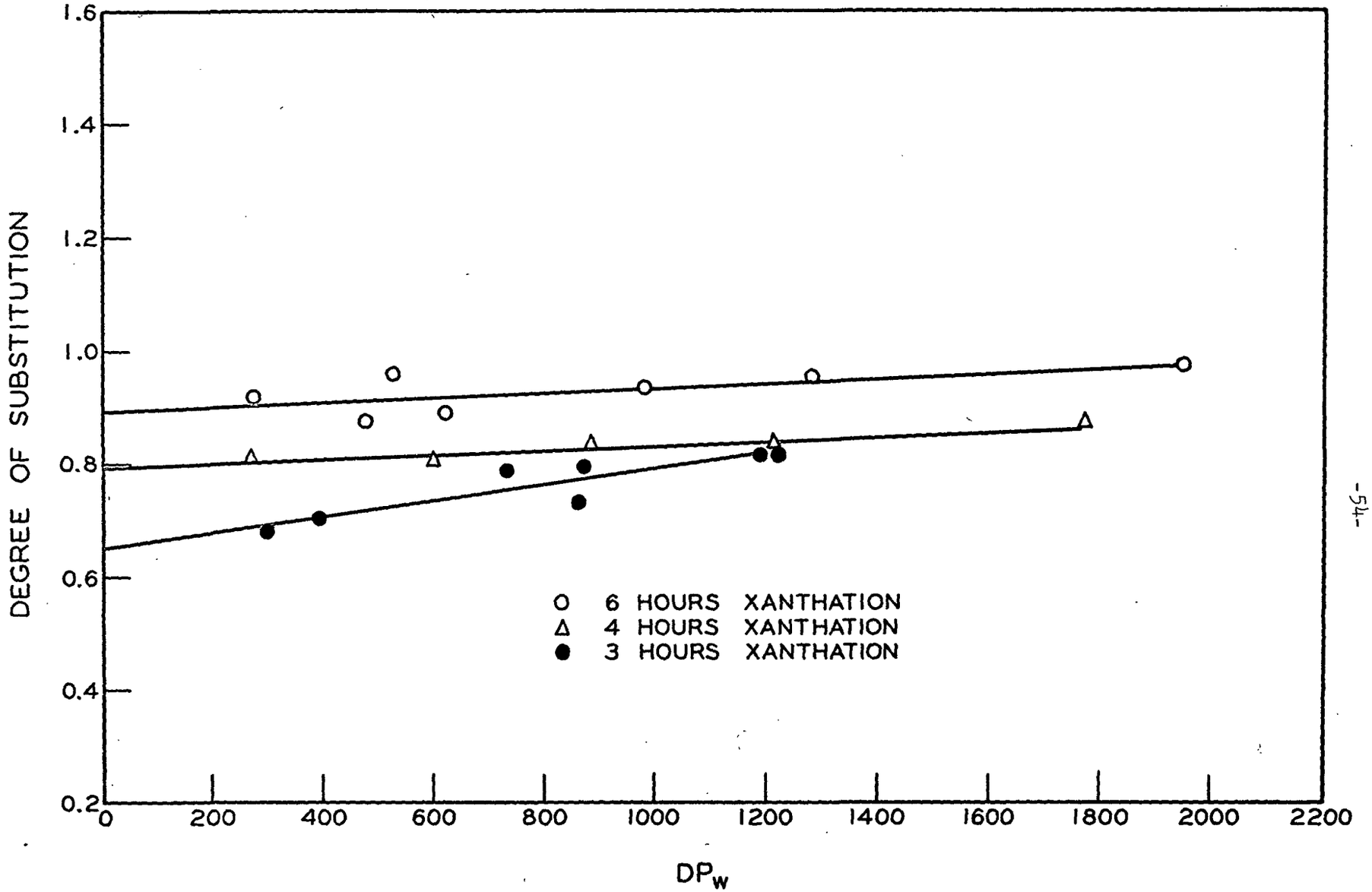

Figure 18. D.S.-D.P. Plot for Viscoses B-3, B-4, and B-6

Viscose B-3 (D.S. = 0.78[a])	$D.S. = (14.49 \times 10^{-5})D.P._w + 0.647$
Viscose B-4 (D.S. = 0.84)	$D.S. = (4.38 \times 10^{-5})D.P._w + 0.790$
Viscose B-6 (D.S. = 0.94)	$D.S. = (4.57 \times 10^{-5})D.P._w + 0.887$

The calculated correlation coefficients are 0.90, 0.92, and 0.70, respectively. The B-3 and B-4 regressions are within the 5% level of significance as determined by the "F" test, while that for B-6 is slightly outside of the 5% level.

It is apparent from the data that the greatest degree of nonuniformity exists during the early stages of xanthation by the emulsion technique. If it had been possible to fractionate the DAX derivative prepared immediately following complete solution of the cellulose xanthate, a value for β somewhat higher than 14.49×10^{-5} would have been anticipated. As indicated by the above results there is an apparent rapid decrease in the nonuniformity of substitution with time. Similar results have been noted for commercial viscose (39).

SUMMARY

Viscose was prepared in the laboratory by the emulsion xanthation technique. The degree of substitution (D.S.) was found to be a linear function of the CS_2:cellulose ratio ($\underline{x}$) for the D.S. range 0.4 to 1.2. This relationship may be expressed as follows:

$$D.S. = 0.259\underline{x} + 0.302$$

Approximately 20-30% of the carbon disulfide was consumed in the formation of the xanthate, while 70-80% existed as free carbon disulfide and sulfur

[a] The D.S. values listed are the average values obtained from the fractionation data.

by-products (principally sodium trithiocarbonate). The total titratable alkali remained essentially constant with increasing amounts of carbon disulfide, while a decrease in the free alkali and an increase in sodium carbonate were noted.

The original degree of polymerization ($D.P._w$) of the viscose-grade cotton linters used in this study was 1135. Degradation was found to be virtually negligible during the six-hour xanthation period. This was in substantial agreement with the claim of Jayme, et al. (54, 55). Slight degradation was, however, noted in the high D.P. portions of the integral distribution curves.

Five viscoses were prepared using CS_2:cellulose ratios ranging from 1.04 to 2.96. The resulting D.S. values of the corresponding xanthates were 0.59, 0.74, 0.95, 1.02, and 1.23. In each case the stable diethylacetamide derivatives were prepared by reaction of the xanthate with diethylchloroacetamide.

Fractionation of a mixed derivative (equal amounts of samples with D.S. values of 0.59 and 0.74) from 70% 2-chloroethanol indicated that fractionation under such conditions was strongly influenced by D.S.

By means of light-scattering measurements, the relationship expressing the k_m constant of the Staudinger equation, $[\eta] = k_m D.P.$, as a function of D.S. was found to be

$$k_m = [5.63 - 3.35 D.S.] \times 10^{-3}$$

Using these relationships, enabled direct calculation of the $D.P._w$ of the DAX fractions from the intrinsic viscosity in 90% dimethyl sulfoxide

and the degree of substitution. Schurz and Armbrüster (6) have recently published a comparable relationship for the k_m constant, using pure dimethyl sulfoxide.

Fractionation of the DAX derivatives of four different D.S. viscoses (0.59, 0.95, 1.02, and 1.23) from aqueous 2-chloroethanol indicated that substitution was somewhat nonuniform with respect to chain length. The deviation from a completely uniform distribution was found to be statistically significant. This phenomenon may be expressed by the following general relationship:

$$D.S. = \beta D.P._w + D.S._o$$

where β and $D.S._o$ are constants that may be related to the xanthation conditions. For the four D.S. levels, β was equal to 5.71×10^{-5}, 4.57×10^{-5}, 4.51×10^{-5}, and 3.37×10^{-5}, respectively. The corresponding $D.S._o$ values were 0.488, 0.887, 0.924, and 1.16, respectively.

Two additional viscoses were prepared for which the xanthation times were three and four hours, as compared with the normal six-hour xanthation period represented by the above samples. The CS_2:cellulose ratio was 1.48. The DAX derivatives were prepared and fractionated from aqueous 2-chloroethanol. The β values for these fractionations were 14.49×10^{-5} (three-hour sample) and 4.38×10^{-5} (four-hour sample). The $D.S._o$ values were 0.647 and 0.790, respectively. The equivalent values for the six-hour xanthation were 4.57×10^{-5} and 0.887.

In summary, two conditions in the emulsion xanthation of cellulose have been considered in light of their influence on the uniformity of substitution, namely the amount of carbon disulfide and the xanthation

time. In all of the cases studied, the longer chains were more highly xanthated than the shorter chains. Indications were that for a constant xanthation time, uniformity improved with increasing amounts of carbon disulfide. On the other hand, for a constant amount of carbon disulfide, uniformity was shown to improve with xanthation time. It was inferred from the data that nonuniformity in substitution would be at a maximum immediately following complete solution of the xanthate. This would correspond to a xanthation time of one-half to two hours, depending upon the amount of carbon disulfide present.

CONCLUSIONS

From this investigation of viscose prepared by the emulsion technique and the corresponding diethylacetamide derivative, the following conclusions can be drawn:

1. The k_m constant, appearing in the Staudinger relationship, is significantly influenced by the degree of substitution (D.S.) of the diethylacetamide derivative. The implication is that with increasing D.S. the molecule becomes more coiled or compact in solution.

2. The fractional precipitation of the diethylacetamide derivative from aqueous 2-chloroethanol is controlled by D.S. where D.S. differences are sufficiently large, e.g., in the fractionation of mixtures of derivatives having significantly different average D.S. values. Where D.S. differences are not significant, fractionation appears to occur according to D.P.

3. For viscose prepared by the emulsion xanthation technique, differences in substitution with respect to chain length exist. Maximum differences exist when small amounts of carbon disulfide and short xanthation times are used. Conversely, the use of large amounts of carbon disulfide and long xanthation times results in a significantly more uniform distribution of the xanthate groups.

4. The fact that the longer cellulose chains are more highly xanthated than the shorter chains leads one to suspect that reaction is primarily molecular in nature. There appears to be a progressive dissolution of the xanthate until solution is complete, i.e., the shorter chains dissolving initially at low degrees of substitution followed by the longer chains at correspondingly higher degrees of substitution. The effects of "after" xanthation are minimized by subsequent hydrolysis or saponification.

THE SOLUTION PROPERTIES OF DIETHYLACETAMIDE CELLULOSE XANTHATE IN DIMETHYL SULFOXIDE

INTRODUCTION

Light-scattering measurements in conjunction with viscosity measurements are particularly useful in determining the molecular properties of high polymers in solution. There appears little need to review the extensive theory that has evolved from the original work of Debye (70). For brief accounts of the theoretical background, the reader is referred to the texts of Flory (71) and Stacey (72).

Scattering of light by molecular solutions arises as a result of existing differences in refractive index between the solute and solvent. For solutions of small particles, the Rayleigh scattering ratio (R_θ), measured at an angle θ, is related to the weight average molecular weight (M_w) of the polymer by the expression,

$$R_\theta = K^*(1 + \cos^2\theta)M_w c \qquad (1)$$

where c is the polymer concentration. The constant, K^*, is evaluated from the following relationship:

$$K^* = 2\pi n_o^2(dn/dc)^2/N\lambda^4 \qquad (2)$$

where

n_o = the refractive index of the solvent,

dn/dc = the refractive index gradient,

N = Avogadro's number, and

λ = the wavelength of the incident light.

For convenience, Equation (1) is expressed in the following form:

$$K^* c/R_{90} = 1/M_w + 2A_2 c + 3A_3 c^2 \qquad (3)$$

where

$\underline{R}_{90}$ = the Rayleigh ratio at 90° and

$\underline{A}_2$ & $\underline{A}_3$ = the virial coefficients.

Expressing Equation (3) in terms of the turbidity, τ, the equation becomes

$$\underline{Hc}/\tau = 1/\underline{M}_w + 2\underline{A}_2\underline{c} + 3\underline{A}_3\underline{c}^2 \qquad (4)$$

where

$$\underline{H} = (32\pi^3/3\lambda^4\underline{N})\underline{n}_o^2(\underline{dn}/\underline{dc})^2 \qquad (5)$$

Applications of the light-scattering technique to solutions of common synthetic polymers (e.g., polystyrene, polymethyl methacrylate, polyvinyl acetate, and polyvinyl alcohol) have been quite extensive. Application to cellulose derivatives has been limited to investigations of the nitrate (52, 73-80), acetate (81), carboxy methyl ether (79, 82), and xanthate (83, 84). No previous data have been reported for the diethylacetamide derivative in solution.

In the presentation that follows it should be noted that two variables, D.P. and D.S., were considered with regard to their influence on the configuration and hydrodynamic parameters. Since the number of samples studied was limited, conclusions with regard to the influence of D.P. and D.S. are indicated only where they appear noteworthy.

NOMENCLATURE

$\underline{a}$	Exponent in the empirical equation relating the intrinsic viscosity and molecular weight, Equation (24).
a	Constant relating the working standard to an opal glass reference standard, Equation (8).

a_1, a_2, a_3	Components of the molecular weight exponent, Equations (25-i), (25-ii), and (25-iii).
A_2, A_3	Virial coefficients appearing in the generalized light scattering equations, Equation (3) *et seq.*
c	Concentration, usually in g./ml. but also in g./100 ml. when used with viscosity measurements, Equation (1) *et seq.*
dn/dc	Refractive index gradient, Equation (2) *et seq.*
F	Product of the transmittances of the neutral filters used in determining the scattering ratio, Equation (8).
G_{90}/G_0	Ratio of the galvanometer reading at 90° to the reading at 0° for the solution, Equation (8).
G'_{90}/G'_0	Ratio of the galvanometer reading at 90° to the reading at 0° for the solvent, Equation (8).
H	Light-scattering constant, Equation (4) *et seq.*
k	Martin constant, Equation (9).
K	Constant in the empirical equation relating intrinsic viscosity and molecular weight, Equation (24).
K*	Parameter relating the Rayleigh scattering ratio to molecular weight, Equations (1)-(3).
L	Path length of the beam in the Rayleigh interferometer, Equations (6) and (7).
M	Fringe displacement, Equations (6) and (7).
M_n, M_w, M_z	Number, weight, and Z- average molecular weights, respectively.
n, n_o	Refractive indexes of the solution and solvent, respectively.
Δn	Refractive index difference between the solution and the solvent, Equation (6).
$P(\theta)$, $Q(\theta)$	Light-scattering functions which depend on the angle θ and the shape of the scattering particle, Equation (11).
$P(90)$	Particle scattering factor at an angle of 90°, Equation (10).
q	Persistence length.

$q\bar{\Phi}$ — Correction factor accounting for the molecular weight heterogeneity, Equations (28) and (29).

$(\bar{r}^2)^{1/2}$, $(\bar{r}_o^2)^{1/2}$ — Root mean square end-to-end length of the perturbed and unperturbed molecule, respectively.

r_{max} — Length of the fully extended polymer chain in solution, commonly referred to as the contour length.

$(\bar{r}_{of}^2)^{1/2}$ — Root mean square end-to-end length of the molecule in solution, assuming free rotation about each single bond of the chain, Equation (23).

R' — Calibration factor relating the narrow diaphragm to the standard diaphragm in the light-scattering photometer, Equation (8).

R_θ, R_{90} — Rayleigh scattering ratios at angle θ and 90°, respectively, Equation (1) et seq.

R_w/R_c — Experimentally determined correction for incomplete compensation of refraction effects, Equation (8).

$(\bar{s}^2)^{1/2}$, $(\bar{s}_o^2)^{1/2}$ — Root mean square radius of gyration of the perturbed and unperturbed molecule, respectively.

x — Number of Porod-Kratky units in the polymer chain.

X — A function related to the molecular expansion factor, Equation (18).

XFX — A function related to the second virial coefficient, Equation (16).

y — Parameter characterizing the molecular weight distribution, Equations (15) and (29).

$[Z]$ — Limiting dissymmetry determined from the ratio of the scattering intensities at 45° and 135° extrapolated to zero concentration.

α — Molecular expansion factor, Equation (18) et seq.

Γ_2 — Second virial coefficient in the generalized light-scattering equation, Equation (13) et seq.

η_{sp}/c — Reduced viscosity, Equation (9).

$[\eta]$ — Intrinsic viscosity, Equation (9).

θ — Angle at which the scattering intensity is measured.

λ — Wavelength of the incident light.

ρ_u Depolarization ratio for unpolarized incident light, Equation (10).

τ Solution turbidity, Equation (4) et seq.

Φ' Asymptotic parameter for flexible polymers, relating the intrinsic viscosity, molecular weight, and the radius of gyration.

$\{\Phi'\}$ Parameter relating the intrinsic viscosity, molecular weight, and the radius of gyration, Equation (25-iii) et seq.

EXPERIMENTAL

LIGHT-SCATTERING APPARATUS

The light-scattering measurements were made using a Brice-Phoenix Light-Scattering Photometer (Series 1937) (85) at a wavelength of 5461 A. A slit width of 4 mm. was used for all measurements.

The apparatus was calibrated by measuring the excess turbidity of a 0.5% solution of Cornell standard polystyrene[a] in toluene. The value of 3.49×10^{-3} cm.$^{-1}$ was in good agreement with the value of 3.51×10^{-3} cm.$^{-1}$ reported in the literature (86).

LIGHT-SCATTERING SAMPLES

Seven samples of the diethylacetamide derivative, covering the D.S. range 0.4-1.2, were selected for study. In each case the samples were fractions isolated by fractional precipitation from a 2-chloroethanol solution, with the exception of Sample 7 which was a composite sample of DAX D (Fractions VII, VIII, IX). The samples are listed in Table XIV.

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[a] The polystyrene sample was obtained through the courtesy of Professor P. Debye, Cornell University, Ithaca, New York.

TABLE XIV

LIGHT-SCATTERING SAMPLES

Sample	Fraction	Nitrogen, %	D.S.	Monomer Molecular Weight
1	DAX A-E-VI	2.35	0.40	238
2	DAX A-X	2.69	0.49	255
3	DAX A-IV	3.04	0.60	275
4	DAX A-E-II	3.56	0.80	313
5	DAX C-VI	3.83	0.92	336
6	DAX C-VIII	3.98	1.00	351
7	DAX D-VII, VIII, IX	4.34	1.22	393

SOLVENT

All light-scattering and viscosity determinations were for solutions of the DAX derivative in a solvent mixture composed of 90% dimethyl sulfoxide-10% water (90 DMSO). The dimethyl sulfoxide was purified by vacuum distillation from calcium hydroxide and stored in the frozen state. The solvent mixture was prepared by adding 10% water by weight. The density of the solvent at 25°C. was 1.099 g./ml.

LIGHT-SCATTERING SOLUTIONS

Complete solution of all DAX fractions in 90% dimethyl sulfoxide was accomplished in less than 24 hours. The solutions were filtered under nitrogen pressure through a sintered-glass filter (max. pore size 2.0-2.5 microns). Two fractions (Samples 3 and 7), that filtered with unusual difficulty, were centrifuged in specially designed cells[a] at

[a] The cells were designed at The Institute of Paper Chemistry specifically for the removal of extraneous dust from light-scattering solutions.

19,000 r.p.m. for 1-1/2 hours in a helium atmosphere. Both techniques adequately removed extraneous dust from the solutions, without changing the solution concentration. Where possible, solutions were transferred directly by filtering into a hemi-octagonal light-scattering cell (Brice-Phoenix D-104); otherwise transfer was performed by use of a pipet. Dilution was accomplished by adding filtered solvent directly to the light-scattering cell until data were obtained for four or five concentrations.

REFRACTIVE INDEX MEASUREMENTS

The refractive index gradient, $\underline{dn}/\underline{dc}$, for the DAX solutions was measured by means of a Rayleigh interferometer (Baird Associates, Cambridge, Mass., Serial Number UA2-19). The instrument was calibrated with aqueous solutions of sucrose.

The difference in refractive index between the solution and pure solvent is related to the number of displaced fringes as follows:

$$\Delta \underline{n} = \underline{M}\lambda/\underline{L} \qquad (6)$$

where

$\underline{M}$ = the number of fringes shifted,

λ = the wavelength of the light source, cm., and

$\underline{L}$ = the path length, cm.

The refractive index gradient was calculated from the following relationship:

$$\underline{dn}/\underline{dc} = \underline{M}\lambda/\underline{L}\Delta\underline{c} \qquad (7)$$

since the number of fringes shifted is linearly related to the concentration change.

Where possible, measurements were made at several concentrations (Appendix III). The refractive index of the solvent (90DMSO) was 1.464.

LIGHT-SCATTERING MEASUREMENTS

Scattering intensities were measured at angles of 0, 45, 90, and 135°. All measurements were made at a temperature of 25° ± 2°C.

A wavelength of 5461 A. was chosen since no significant fluorescence could be detected for the DAX solutions at this wavelength; whereas, at a wavelength of 4358 A., fluorescence led to scattering ratios approximately 15% too high.

The limiting dissymmetry, [Z], was evaluated in the usual manner by extrapolation of $1/(Z - 1)$ to zero concentration (87). The dissymmetry value thus obtained was corrected for internally reflected light (Appendix IV). The reciprocal particle-scattering factor, $1/P(\theta)$, and the root mean square end-to-end length, $(\bar{r}^2)^{1/2}$, were obtained from the appropriate tables calculated by Doty and Steiner (88) for randomly coiled molecules in solution.

The depolarization correction was evaluated by extrapolation of $(6 + 6\rho_u)/(6 - 7\rho_u)$ to zero concentration (89). The depolarization, ρ_u, is the ratio of the horizontal component to the vertical component measured at 90° for unpolarized incident light (Appendix IV).

Correction for selective absorption at a wavelength of 5461 A. was found to be unnecessary.

The absolute turbidity, τ, in cm.$^{-1}$ at an angle θ and a solution concentration, c, was calculated from the following relationship:

$$\tau\ (\theta, c) = 1.21R'\ (n_o^2 R_w/R_c)\ a\ F\ [(G_{90}/G_o)-(G'_{90}/G'_o)]\ [\sin\theta/(1 + \cos^2\theta)] \qquad (8)$$

where

R' = the calibration factor relating the narrow diaphragm (4 mm.) with the standard diaphragm (12 mm.),

n_o = the refractive index of the solvent,

R_w/R_c = the experimentally determined correction for incomplete compensation of refraction effects,

a = the constant relating the working standard to an opal glass reference standard,

F = the product of the transmittances of the neutral filters used in determining the scattering ratio,

G_{90}/G_o = the ratio of the galvanometer reading at 90° to the reading at 0° for the solution,

G'_{90}/G'_o = the ratio of the galvanometer reading at 90° to the reading at 0° for the solvent, and

$\sin\theta/(1 + \cos^2\theta)$ = the factor accounting for the angular dependence of the scattering volume.

The factor, R', was equal to 1.06 for all samples except Sample 5. In this case, R' was equal to 1.25. The difference in these values resulted from a change in the photometer light source. The value of $n_o^2 R_w/R_c$ for 90% dimethyl sulfoxide was 2.352. The constant a was checked periodically and ranged from 0.611 to 0.622.

The molecular weight (uncorrected for dissymmetry and depolarization) was determined from Equation (4) by extrapolation of $Hc/\tau\ (90°, c)$, measured at four or more concentrations, to zero concentration.

VISCOSITY MEASUREMENTS

The intrinsic viscosities, $[\eta]$, were determined by extrapolation of the log (η_{sp}/c) versus c plot to zero concentration according to

the Martin equation (62).

$$\log (\eta_{sp}/c) = \log[\eta] + k [\eta]c \qquad (9)$$

The reduced viscosities in 90% dimethyl sulfoxide were determined at 25° ± 0.02°C. using an Ubbelohde dilution viscometer. Both shear and kinetic energy corrections were found to be negligible. The shear rate for all measurements was 550 ± 25 sec.$^{-1}$.

PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

TURBIDITY DATA

The turbidity data are summarized in Table XV, and the corresponding Hc/τ plots are shown in Fig. 19. The extrapolated values, Hc/τ (90°, 0°), are given in Table XVI, along with the limiting dissymmetry, the reciprocal particle-scattering factor, the depolarization, and the reciprocal of the Cabannes factor.

The molecular weights, M_w, recorded in Table XVI were calculated from the following relationship:

$$M_w = [Hc/\tau\,(90°, 0°)]^{-1}[1/P(90)][(6 - 7\rho_u)/(6 + 6\rho_u)] \qquad (10)$$

The estimated error in M_w is approximately 10% (52).

VISCOSITY DATA

The viscosity data are shown in Table XVII. The intrinsic viscosities were obtained from Fig. 20 and are listed in Table XVI.

The average value for the Martin constant (k) was 0.17, which corresponds to the usual range of values (0.15-0.25) reported for cellulose nitrate and cellulose acetate in suitable solvents (62). Average

TABLE XV

TURBIDITY DATA - FRACTIONATED DAX SAMPLES

	Concn., g./ml. x 10^2	τ, cm.$^{-1}$ x 10^4	Hc/τ (90°,c) x 10^6	$[Hc/\tau$ (0°,c)$]^{1/2}$ x 10^3
Sample 1	0.289	2.66	29.7	4.34
D.S. = 0.40	0.224	2.46	25.1	4.03
	0.177	2.22	21.9	3.79
	0.149	2.04	20.0	3.63
Sample 2	0.324	3.14	13.1	2.85
D.S. = 0.49	0.264	2.78	12.0	2.75
	0.221	2.47	11.4	2.68
	0.188	2.10	11.3	2.67
	0.164	1.89	11.0	2.65
Sample 3	0.206	6.78	8.31	2.00
D.S. = 0.60	0.134	5.06	7.20	1.87
	0.112	4.27	7.14	1.88
	0.094	3.66	7.00	1.87
Sample 4	0.360	11.74	8.39	2.10
D.S. = 0.80	0.199	7.76	7.04	1.94
	0.151	5.98	6.88	1.93
	0.122	5.23	6.40	1.93
Sample 5	0.244	9.04	4.43	1.74
D.S. = 0.92	0.199	7.90	4.12	1.68
	0.171	7.13	3.92	1.63
	0.143	6.15	3.81	1.61
Sample 6	0.393	8.52	5.63	1.94
D.S. = 1.00	0.320	7.52	5.18	1.86
	0.268	6.68	4.90	1.81
	0.223	6.04	4.51	1.74
	0.184	5.00	4.50	1.74
Sample 7	0.360	18.2	5.42	1.94
D.S. = 1.22	0.288	15.8	4.97	1.87
	0.232	12.7	4.76	1.84
	0.184	11.5	4.36	1.78

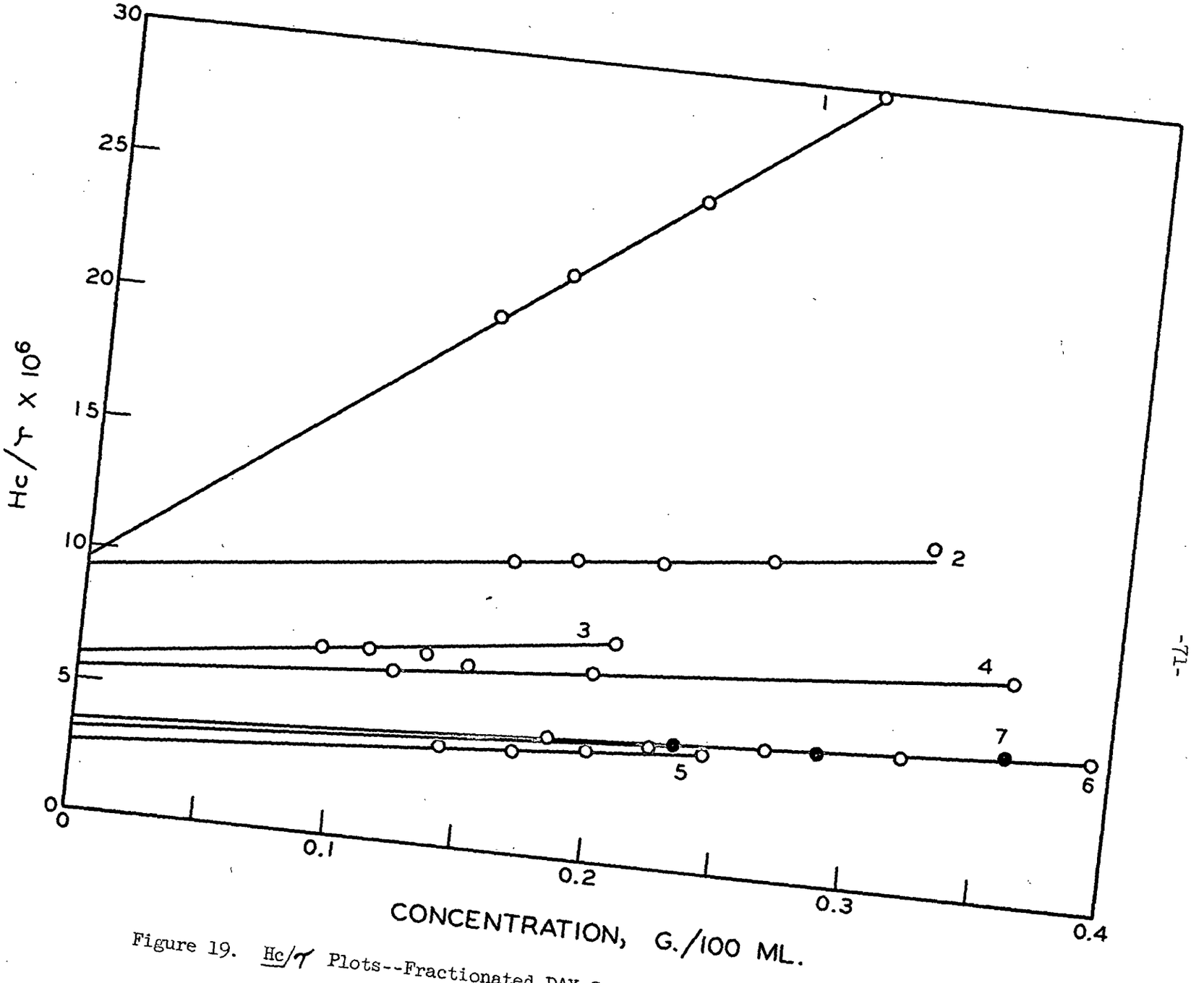

Figure 19. Hc/τ Plots--Fractionated DAX Samples in 90% Dimethyl Sulfoxide

TABLE XVI

SUMMARIZED LIGHT-SCATTERING DATA

Sample	1	2	3	4	5	6	7
D.S.	0.40	0.49	0.60	0.80	0.92	1.00	1.22
Monomer mol. wt.	238	255	275	313	336	351	393
$\overline{dn/dc}$[a]	0.1435	0.0977	0.1435	0.1435	0.0977	0.0960	0.0791
$\overline{Hc/\tau}(90°,0) \times 10^6$	9.62	9.21	5.89	5.48	2.88	3.50	3.26
$(\overline{M}_w)_{uncorr.} \times 10^{-5}$	1.04	1.09	1.70	1.83	3.48	2.86	3.37
$(\overline{D.P.}_w)_{uncorr.}$	437	426	618	583	1035	815	857
$[Z]$[b]	1.35	1.51	2.29	1.72	1.43	1.45	1.45
$1/\overline{P}(90)$[c]	1.25	1.37	1.89	1.56	1.31[g]	1.33	1.33
$[\overline{\rho_u}]$[d]	0.067	0.064	0.039	0.067[g]	0.058[g]	0.048	≤ 0.01
$(6-7\rho_u)/(6+6\rho_u)$[e]	0.86	0.87	0.98	0.86	0.88	0.89	1.00
$\overline{M}_w \times 10^{-5}$	1.12	1.29	3.16	2.45	4.01	3.40	4.46
$\overline{D.P.}_w$	473	506	1150	781	1190	969	1130
$[\eta]_{90DMSO}$	1.79	2.31	4.40	2.44	2.67	1.89	2.04
Martin constant, k	0.11_9	0.15_4	0.17_6	0.20_5	0.14_9	0.16_2	0.19_2
$k_m \times 10^4$[f]	37.9	45.6	38.0	31.6	22.5	19.6	18.0

[a] Refractive index gradient.
[b] Dissymmetry ratio at zero concentration.
[c] Reciprocal particle-scattering factor.
[d] Depolarization factor for unpolarized incident light at zero concentration.
[e] Reciprocal of the Cabannes factor.
[f] $k_m = [\eta]/D.P._w$
[g] Assumed values.

TABLE XVII

VISCOSITY DATA - FRACTIONATED DAX SAMPLES

	Concn., g./dl.	η_{sp}/c, dl./g.
Sample 1	0.289	2.06
D.S. = 0.40	0.193	2.00
$[\eta]$ = 1.79	0.145	1.90
	0.116	1.89
Sample 2	0.371	3.25
D.S. = 0.49	0.247	2.99
$[\eta]$ = 2.31	0.185	2.84
	0.148	2.70
Sample 3	0.365	8.43
D.S. = 0.60	0.244	6.84
$[\eta]$ = 4.40	0.183	6.15
	0.146	5.77
Sample 4	0.360	3.69
D.S. = 0.80	0.240	3.22
$[\eta]$ = 2.44	0.180	3.02
	0.144	2.89
Sample 5	0.295	3.53
D.S. = 0.92	0.197	3.20
$[\eta]$ = 2.67	0.148	3.06
	0.118	2.91
Sample 6	0.422	2.55
D.S. = 1.00	0.282	2.30
$[\eta]$ = 1.89	0.211	2.20
	0.169	2.12
Sample 7	0.180	2.40
D.S. = 1.22	0.120	2.30
$[\eta]$ = 2.04	0.090	2.22
	0.072	2.15

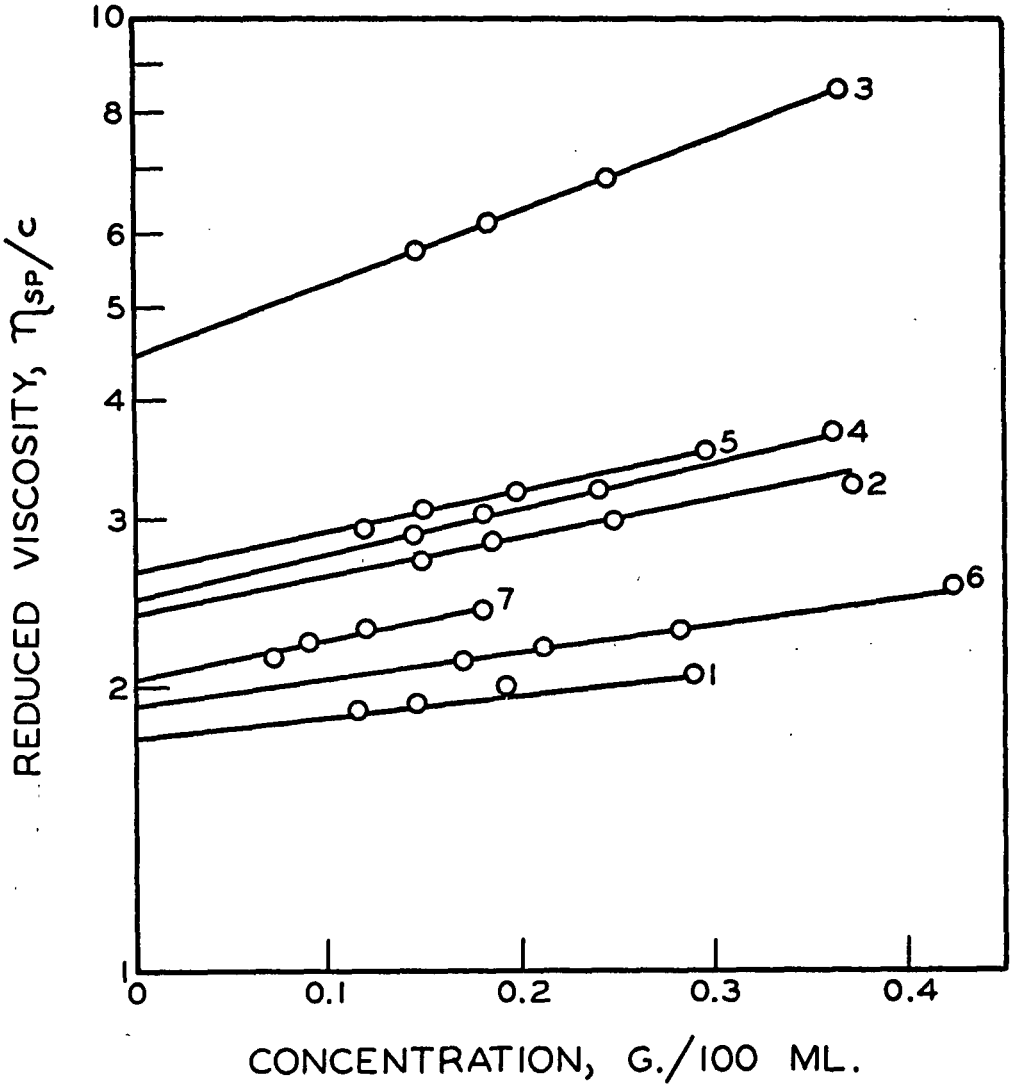

Figure 20. Viscosity Data--Fractionated DAX Samples in 90% Dimethyl Sulfoxide

values for the Martin constant calculated from the previously reported fractionation data are as follows:

DAX A (in 90 DMSO) = 0.15_5
DAX B (in 90 DMSO) = 0.16_4
DAX C (in 90 DMSO) = 0.17_4
DAX D (in 70 ECH) = 0.17_9

The Martin constant increases with increasing D.S. This variation may be interpreted as corresponding to a decrease in solvation with increasing D.S. This effect shows up in the negative slope of the k_m versus D.S. plot (Fig. 8). This conclusion substantiates the contention of Trieber, et al. (37) that dimethyl sulfoxide is a good solvent for low D.S.-diethylacetamide cellulose xanthate.

DETERMINATION OF THE SECOND VIRIAL COEFFICIENT

According to Zimm (90), the light-scattering equation for large molecules may be written in the following form:

$$\underline{Hc}/\tau(\theta, \underline{c}) = 1/\underline{M}_w\underline{P}(\theta) + 2\underline{A}_2\underline{c} + \left\{3\underline{A}_3\underline{Q}(\theta) - 4\underline{A}_2^2\underline{P}(\theta)\,[1 - \underline{P}(\theta)]\right\}\underline{c}^2 + \cdots \qquad (11)$$

where

$\underline{A}_2$ & $\underline{A}_3$ = the second and third virial coefficients, respectively, and

$\underline{P}(\theta)$ & $\underline{Q}(\theta)$ = functions dependent upon the angle θ and the properties of the molecule.

When θ is equal to zero degrees, both $\underline{P}(\theta)$ and $\underline{Q}(\theta)$ become equal to unity, reducing Equation (11) to the following form:

$$\underline{Hc}/\tau(0°, \underline{c}) = (1/\underline{M}_w)(1 + 2\underline{A}_2\underline{M}_w\underline{c} + 3\underline{A}_3\underline{M}_w\underline{c}^2) \qquad (12)$$

According to Flory, et al. (52), $\underline{A}_2$ may be set equal to $\Gamma_2/\underline{M}_w$; where Γ_2 corresponds to the second virial coefficient in the generalized osmotic pressure relationship. Since $\underline{A}_3$ is approximately equal to $\Gamma_2^2/4\underline{M}_w$, Equation (12) becomes

$$\underline{Hc}/\tau(0°, \underline{c}) = [\underline{Hc}/\tau(0°, 0)][1 + 2\Gamma_2\underline{c} + 3\Gamma_2^2\underline{c}^2/4] \quad (13)$$

Taking the square root of both sides, leads to the satisfactory approximation represented by Equation (14).

$$[\underline{Hc}/\tau(0°, \underline{c})]^{1/2} \backsim [\underline{Hc}/\tau(0°, 0)]^{1/2}[1 + \Gamma_2\underline{c}] \quad (14)$$

Plotting $[\underline{Hc}/\tau(0°, \underline{c})]^{1/2}$ versus concentration in the manner of Flory, et al. (52) enabled evaluation of both $\underline{A}_2$ and Γ_2 (Fig. 21). The calculated values of $[\underline{Hc}/\tau(0°, \underline{c})]^{1/2}$, corrected for dissymmetry and depolarization, are shown in Table XV. A more rigorous evaluation would require extrapolation to zero angle.

The second virial coefficient, $\underline{A}_2$, is an indirect measure of polymer-solvent interaction, since it depends principally upon the size of the polymer coil and the affinity of the polymer for the solvent. Low values are an indication of preferential polymer-polymer contacts; whereas, high values indicate highly solvated molecules (91).

The unusually high value of the second virial coefficient for Sample I was somewhat questionable, considering the other values shown in Table XVIII. It appeared, however, that below a D.S. of 0.8 the derivative was more solvated than at the higher D.S. levels. As a direct consequence, the degree of coiling or compactness of the molecule would be higher in the D.S. range 0.8-1.22.

Figure 22 shows the relationship between the second virial coefficient, Γ_2, and the molecular weight. For purposes of comparison, the data of Flory, et al. (52) are also shown. Over the same molecular weight range, Γ_2 for the diethylacetamide derivative was considerably less influenced by molecular weight. Indications were that the diethylacetamide derivative is considerably more coiled in solution than cellulose nitrate.

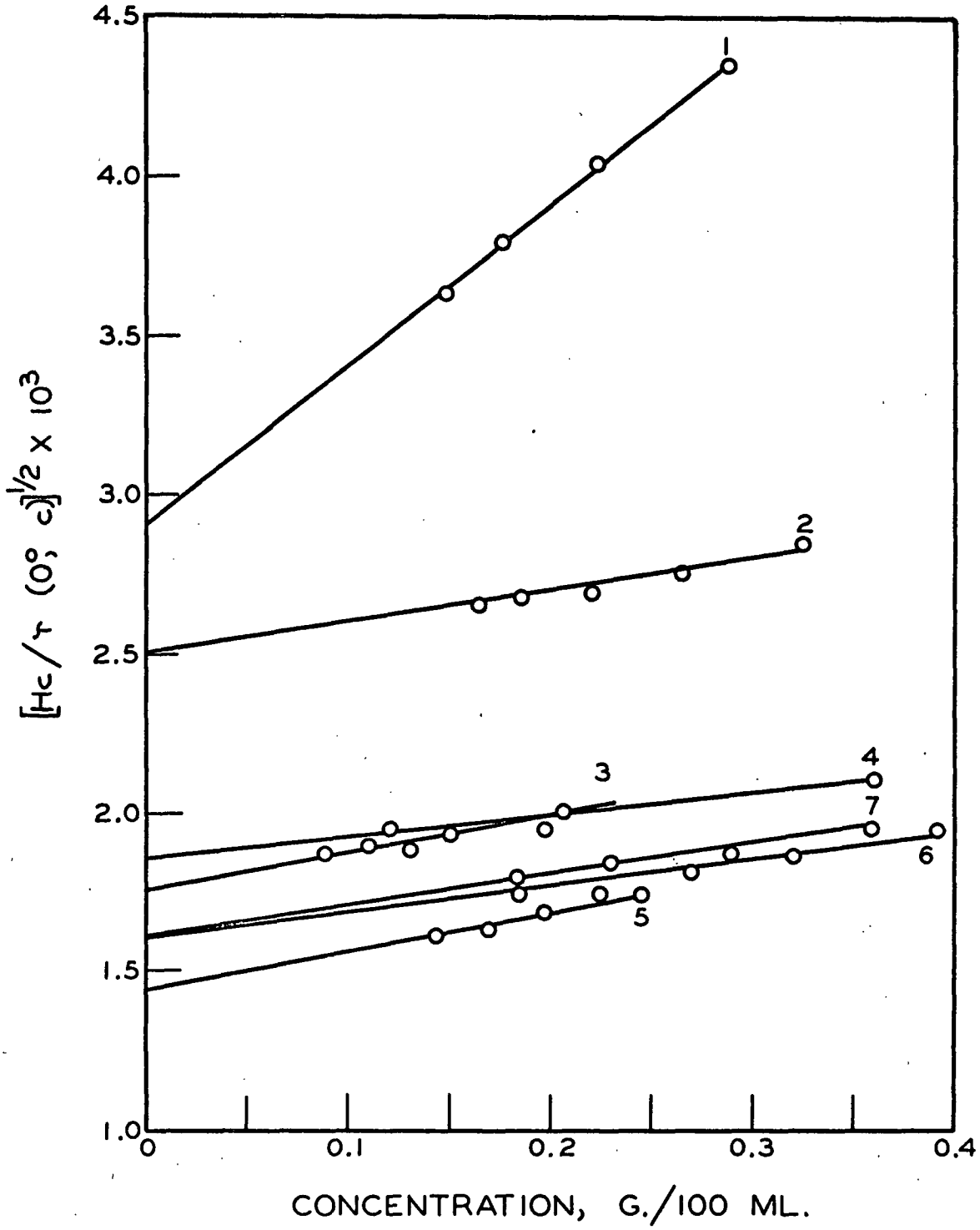

Figure 21. Light-Scattering Data at $\theta = 0°$ for Fractionated DAX Samples

TABLE XVIII

CALCULATED SECOND VIRIAL COEFFICIENTS

Sample	D.S.	A_2, mole cc. $g.^{-2}$ x 10^5	Γ_2, cc./g.
1	0.40	147.	171.
2	0.49	23.1	37.2
3	0.60	19.0	60.6
4	0.80	11.1	32.1
5	0.92	15.4	71.0
6	1.00	12.4	47.3
7	1.22	16.3	65.6

Note: Γ_2 was computed from the slopes of the $[Hc/\tau\ (0°, c)]^{1/2}$ versus concentration plots shown in Fig. 21. A_2 was calculated directly from the Γ_2 value. The unusually high values for these coefficients in the case of Sample 1 appear subject to some question. The errors in Γ_2 and A_2 are estimated at ± 15%, since it was necessary to assume values for the depolarization correction in the case of Samples 2, 4, and 5.

MOLECULAR WEIGHT DISTRIBUTION

For purposes of interpretation, it was necessary to make certain assumptions as to the molecular heterogeneity of the fractions. Polydispersity is inevitable even for carefully fractionated material. The molecular weight distribution for polymers may be represented in the following manner:

$$M_z : M_w : M_n = (y + 2) : (y + 1) : y \qquad (15)$$

where y is evaluated from the M_w/M_n ratio. The anticipated range of values for the M_w/M_n ratio based on the theory of fractionation is 1.5-2.0 (92). For a molecular weight range similar to that considered here, Flory, et al. (52) have reported ratios ranging from 1.5 to 2.2 for

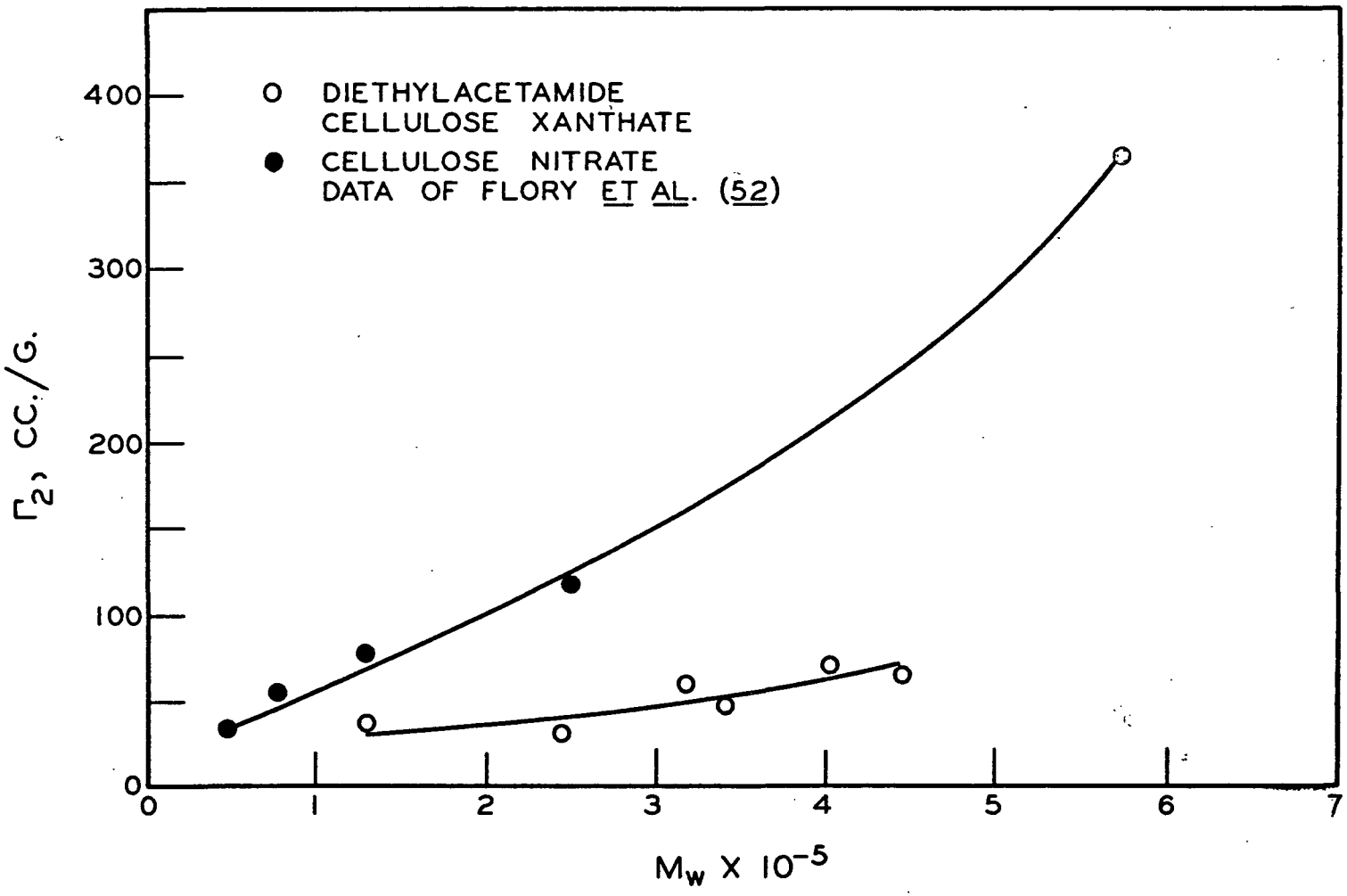

Figure 22. Variation of the Second Virial Coefficient, Γ_2, with Molecular Weight ($\underline{M}_w$).

fractionated cellulose nitrate. For this work a 3:2:1 distribution ($\underline{M}_z:\underline{M}_w:\underline{M}_n$) was assumed. Such a distribution has been assumed by others in similar studies (52, 78, 80, 90).

CONFIGURATION PARAMETERS

Expansion Factor, α

The expansion factor, α, which accounts for the influence of the density of the elements within the effective volume of the molecule and the interaction of the elements with the solvent, was calculated according to the method of Orofino and Flory (93) from the following relationships:

$$\Gamma_2 = 4(\pi/3)^{3/2}\underline{N}\,\underline{M}_w^{1/2}(\bar{\underline{s}}^2/\underline{M}_w)^{3/2}\underline{XFX} \qquad (16)$$

$$\underline{XFX} = (4/\pi^{1/2})\ln[(\pi^{1/2}/4)\underline{X} + 1] \qquad (17)$$

$$\underline{X} = 2(\alpha^2 - 1) \qquad (18)$$

where $\underline{N}$ is Avogadro's number. The calculated values of α, shown in Table XIX, ranged from 1.01 to 1.12. There appeared to be a slight increase in α with molecular weight. Flory, et al. (52) reported an average value of 1.04 for cellulose nitrate in ethyl acetate, while Huque, et al. (80) reported values ranging from 1.03 to 1.09 for the nitrate in both ethyl acetate and acetone.

Root Mean Square End-to-End Length

The root mean square end-to-end length, $(\bar{\underline{r}}^2)^{1/2}$, was calculated from the experimentally determined limiting dissymmetry, using the tables of Doty and Steiner (88) for a random coil configuration. These

TABLE XIX

CONFIGURATION PARAMETERS FOR DIETHYLACETAMIDE CELLULOSE XANTHATE IN 90% DIMETHYL SULFOXIDE

Sample	1	2	3	4	5	6	7
D.S	0.40	0.49	0.60	0.80	0.92	1.00	1.22
$\underline{M}_w \times 10^{-5}$	1.12	1.29	3.16	2.45	4.01	3.40	4.46
$\underline{M}_z \times 10^{-5}$	1.68	1.93	4.74	3.67	6.01	5.10	6.69
D.P.$_w$	473	506	1150	781	1190	969	1130
D.P.$_z$	706	757	1720	1170	1790	1450	1700
Expansion factor, α	1.10	1.02	1.02	1.01	1.12	1.07	1.10
$(\bar{r}^2)^{1/2}$, A.	864	1030	1555	1245	934	980	980
$(\bar{r}_o^2)^{1/2}$, A.	786	1010	1520	1230	834	915	890
$(r_{max})_z$, A.	3630	3890	8840	5500	9200	7450	8730
$(\bar{s}^2)^{1/2}$, A.	352	420	634	510	380	400	400
$(\bar{s}_o^2)^{1/2}$, A.	319	412	631	504	339	374	363
$(\bar{r}_o^2)^{1/2}/(r_{max})_z$	0.22	0.26	0.17	0.22	0.09	0.12	0.10
$(\bar{r}^2/\text{D.P.}_w)^{1/2}$, A.	39.6	45.6	45.8	44.5	27.1	31.2	29.1
Persistence length, A.	84	131	135	138	35	55	45
$(\bar{r}_{of}^2)^{1/2}$, A.	171	179	268	221	272	246	266
$(\bar{r}^2)^{1/2}/(\bar{r}_{of}^2)^{1/2}$	4.60	5.63	5.68	5.56	3.06	3.71	3.34

values are shown in Table XIX, along with the unperturbed end-to-end length, $(\bar{r}_o^2)^{1/2}$. The latter values were calculated from the relationship

$$(\bar{r}^2)^{1/2} = \alpha(\bar{r}_o^2)^{1/2} \qquad (19)$$

Doty, et al. (77) have suggested that a Gaussian random coil configuration may justifiably be assumed when the ratio of the end-to-end length to the contour length[a] is less than one-third. Figure 23 shows the calculated $(\bar{r}_o^2)^{1/2}/r_{max}$ values as a function of the weight average molecular weight. The data of Flory, et al. (52) and Holtzer, et al. (78) for cellulose nitrate, and Mandelkern and Flory (94) for cellulose tributyrate are also shown in Fig. 23. The diethylacetamide derivative apparently qualifies as a random coil in the molecular weight range represented by the samples.

Root Mean Square Radius of Gyration

The radius of gyration of a coiled molecule in solution is defined as the average radius of all the elements from the center of mass of the molecule. For a random coil it is related to the end-to-end length as follows:

$$(\bar{s}^2) = (\bar{r}^2)/6 \qquad (20)$$

The radius of gyration thus calculated is related to the unperturbed radius of gyration, $(\bar{s}_o^2)^{1/2}$, as follows:

$$(\bar{s}^2)^{1/2} = \alpha\,(\bar{s}_o^2)^{1/2} \qquad (21)$$

The calculated values for $(\bar{s}^2)^{1/2}$ and $(\bar{s}_o^2)^{1/2}$ are given in Table XIX.

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[a] Contour length = r_{max} = D.P. x 5.15A.

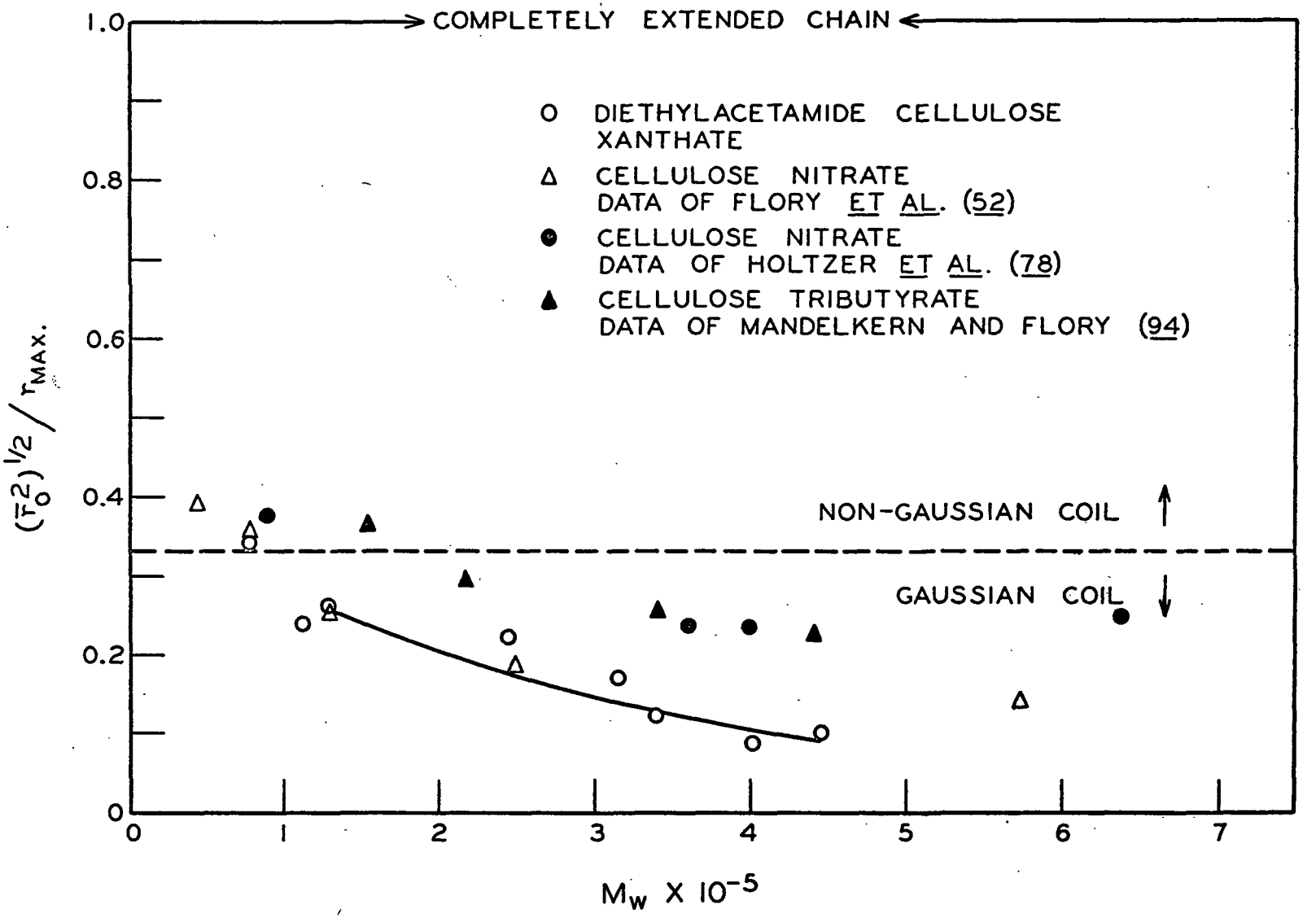

Figure 23. Ratio of Root Mean Square End-to-End Length, $(\bar{r}_o^2)^{1/2}$, to Maximum Length, r_{max}, versus Molecular Weight (M_w)

Restrictions on Free Rotation

For cellulose derivatives, free rotation is only possible about the ether linkages. Rotation at these points is, however, restricted by both the valence angle and steric hindrance. For this reason the use of random-flight statistics to determine the molecular dimensions must be limited to molecules sufficiently long to approximate a freely jointed chain.

The effective bond length[a], as suggested by Doty (77, 78) is the bond length of a hypothetical freely jointed analog, possessing no restrictions by valence angle or steric hindrance to coiling. This hypothetical chain possesses the same number of bonds as the chain under consideration, and hence possesses a much longer contour length. Doty, et al. (78) have reported an effective bond length for cellulose nitrate of 35 A. Flory, et al. (52) and Munster (95) have verified this value. The average of the values reported in Table XIX for the DAX derivative is 37 A., which corresponds to somewhat over seven glucose units. Free rotation, therefore, is considerably hindered. Common synthetic polymers exhibit appreciably greater flexibility in solution, having effective bond lengths less than 10 A.

Kratky and Porod (96) have suggested another method for evaluating the restriction on free rotation. In this case the persistence length, q, is defined as the integral length of the average projection of the elements of an infinitely long chain in the direction of the initial element of the chain. The persistence lengths, calculated according

[a] Effective bond length in A. $= (\bar{r}^2/\text{D.P.})^{1/2}$ (22)

to the method of Benoit and Doty (97), are shown in Table XIX. The average value for Samples 2, 3, and 4 was 135 A., which corresponded reasonably with the value of 117 A. reported for cellulose nitrate in ethyl acetate.

If rotation about ether linkages was unhindered, the theoretical mean square end-to-end length, $\bar{r}_{of}^2$, might be calculated from the following relation, which holds for all cellulose derivatives (98):

$$\bar{r}_{of}^2 = 62.4 \text{ D.P.} \qquad (23)$$

The value $(\bar{r}_o^2/\bar{r}_{of}^2)^{1/2}$ is a measure of the higher molecular extension expected if rotation about the ether linkages is restricted. This value as indicated in Table XIX ranges from 3.06 to 5.68. Mandelkern and Flory (94) have reported that this value for cellulose tributyrate increases from 3.1 to 3.5 over the molecular weight (M_n) range 77,000 to 220,000. Similar values calculated for cellulose nitrate from the data of Flory, et al. (52) ranged from 3.37 to 4.30 for the molecular weight (M_w) range 41,000 to 573,000.

HYDRODYNAMIC PARAMETERS

The molecular weight of long-chain polymers in solution may be estimated from viscosity measurements by means of the Mark-Houwink form of the Staudinger equation,

$$[\eta] = KM^a \qquad (24)$$

where the exponent a may be separated into the following contributing factors (52):

$$a = 0.5 + 3a_1 + 1.5a_2 + a_3 \qquad (25)$$

in which

$$\underline{a}_1 = d\ln\alpha/d\ln\underline{M} \qquad (25\text{-i})$$

$$\underline{a}_2 = d\ln(\underline{\bar{s}}_o^2/\underline{M})/d\ln\underline{M} \qquad (25\text{-ii})$$

$$\underline{a}_3 = d\ln\{\Phi\}/d\ln\underline{M} \qquad (25\text{-iii})$$

For common flexible polymers, $\underline{a}_2$ and $\underline{a}_3$ are negligible, while $\underline{a}_1$ will have a value of approximately 0.1. For such polymers the maximum value of $\underline{a}$ is 0.8. For cellulose derivatives, $\underline{a}_1$ is negligible, while $\underline{a}_2$ and/or $\underline{a}_3$ contribute appreciably to the intrinsic viscosity. Values of $\underline{a}$ significantly higher than 0.8 have been reported for such derivatives.

As shown in Table XIX, the molecular expansion factor (α) appeared to increase slightly with molecular weight. The high value for Sample 1 was attributed to the questionable value obtained for the second virial coefficient. Increasing D.S. would be expected to be responsible for a part of this increase in α; however, neglecting this consideration, the calculated value of $\underline{a}_1$ was 0.007. The effective contribution of this increase in α to the intrinsic viscosity is negligible.

The value of $\underline{a}_2$ was estimated from the following relationship (52):

$$\underline{a}_2 \cong 3(1 - 4/\underline{x} + 6/\underline{x}^2)/\underline{x}(1 - 3/\underline{x} + 6/\underline{x}^2 - 6/\underline{x}^3) \qquad (26)$$

where $\underline{x}$ was the weight average number of Porod-Kratky units per molecule. The calculated values for Samples 1-7 were 0.10, 0.14, 0.07, 0.11, 0.03, 0.02, and 0.02. These values are shown as a function of $\underline{M}_w$ in Fig. 24. Also shown are the values reported by Flory, et al. for cellulose nitrate (52). The agreement is rather striking. The effective value of $\underline{a}_2$ at the middle of the molecular weight range is 0.08, corresponding to an exponent contribution of 0.12.

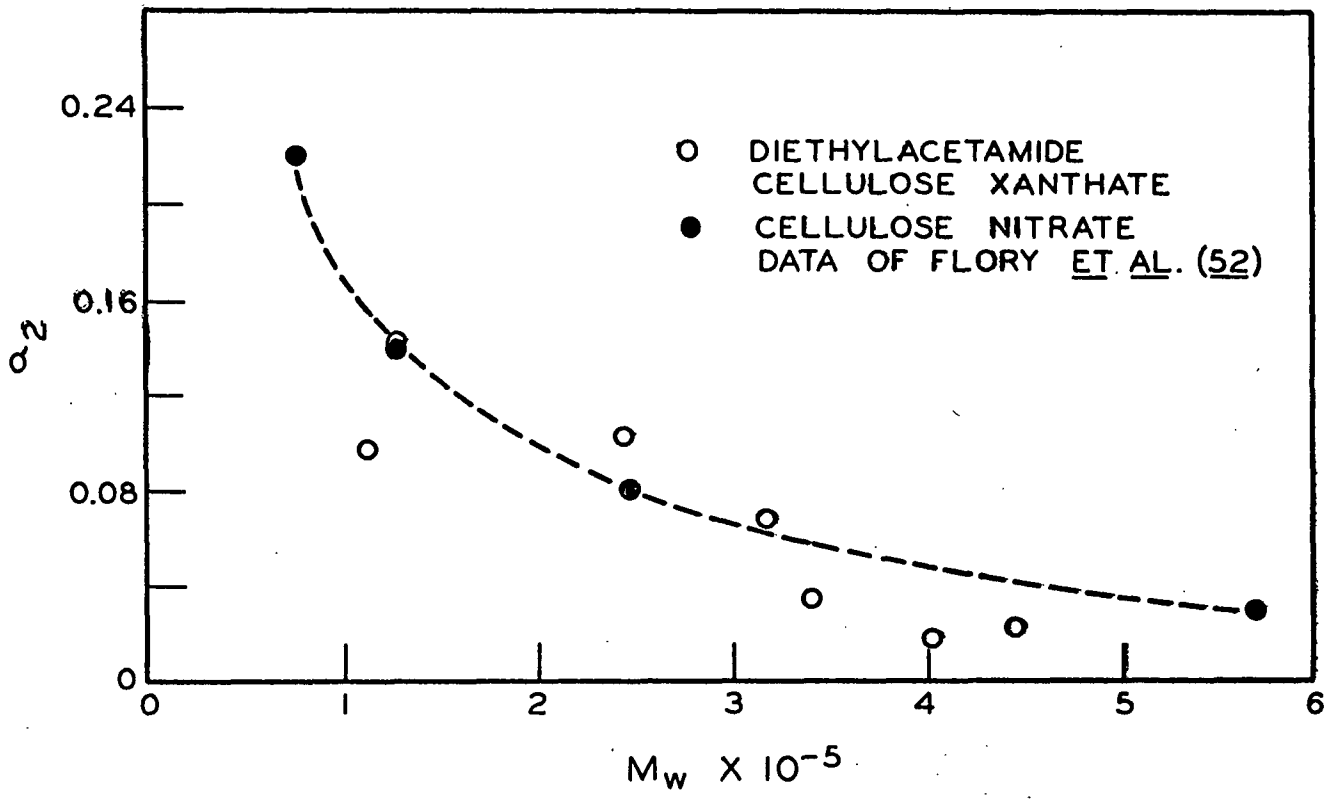

Figure 24. Variation of a_2 with Molecular Weight (M_w)

The remaining contribution to the exponent a is the variation in the hydrodynamic parameter, $\{\Phi'\}^a$. For flexible polymers in solution, Φ' has been found to be approximately 3.2×10^{22}, which is somewhat less than the theoretical value predicted by the Kirkwood-Riseman theory (99) for such polymers.

According to the Fox-Flory theory (100), the intrinsic viscosity, radius of gyration, and the molecular weight are related as follows:

$$[\eta] = \Phi' (\bar{s}^2)^{3/2}/M \qquad (27)$$

[a] The brackets differentiate this value from the asymptotically constant value, Φ', which holds for more flexible polymers.

Introducing the factor q_Φ, as suggested by Flory, et al. (52), to account for the effects of molecular weight heterogeneity, Equation (27) may be written in the following form:

$$\{\Phi'\} = q_\Phi [\eta] M_w/(\bar{s}^2)^{3/2} \qquad (28)$$

The change in $[\eta] M_w/(\bar{s}^2)^{3/2}$, calculated from the data in Table XVI, with molecular weight is shown in Fig. 25. Also shown are similar values determined for cellulose nitrate (52). It must be remembered that each of the points for the DAX derivatives represents a point on the curve for that particular D.S. In actuality there would be expected to exist a series of curves for each D.S. in the range under consideration. The data available, however, do not permit the construction of such curves. As indicated by the radii of gyration data in Table XIX and the k_m versus D.S. plot shown in Fig. 8, there appeared to be a significant increase in the degree of coiling of the molecule with D.S. This would be reflected by an increase in $[\eta] M_w/(\bar{s}^2)^{3/2}$ with D.S. An increase in D.P. would also result in an increase in this ratio, although the effect would be to some extent counterbalanced by an increase in $(\bar{s}^2)^{3/2}$.

The factor q_Φ, was calculated from the following expression (52):

$$q_\Phi = [\Gamma(y + 3 + 2a_1 + a_2)]^{3/2} (y + 1)^{-2} [\Gamma(y + 2)]^{-1/2} [\Gamma(y + 3/2 + 3a_1 + 3a_2/2)]^{-1} \qquad (29)$$

The values of q_Φ have been calculated for both $y = 1$ and $y = 2$. These values of y correspond to M_w/M_n ratios of 1.5 and 2.0, respectively [see Equation (15)]. The corresponding values of $\{\Phi'\}$ were calculated for these values of y and are shown in Table XX. It appears that this value approaches the theoretical asymptotic value for the high D.S. samples (>0.90) at molecular weights above 400,000.

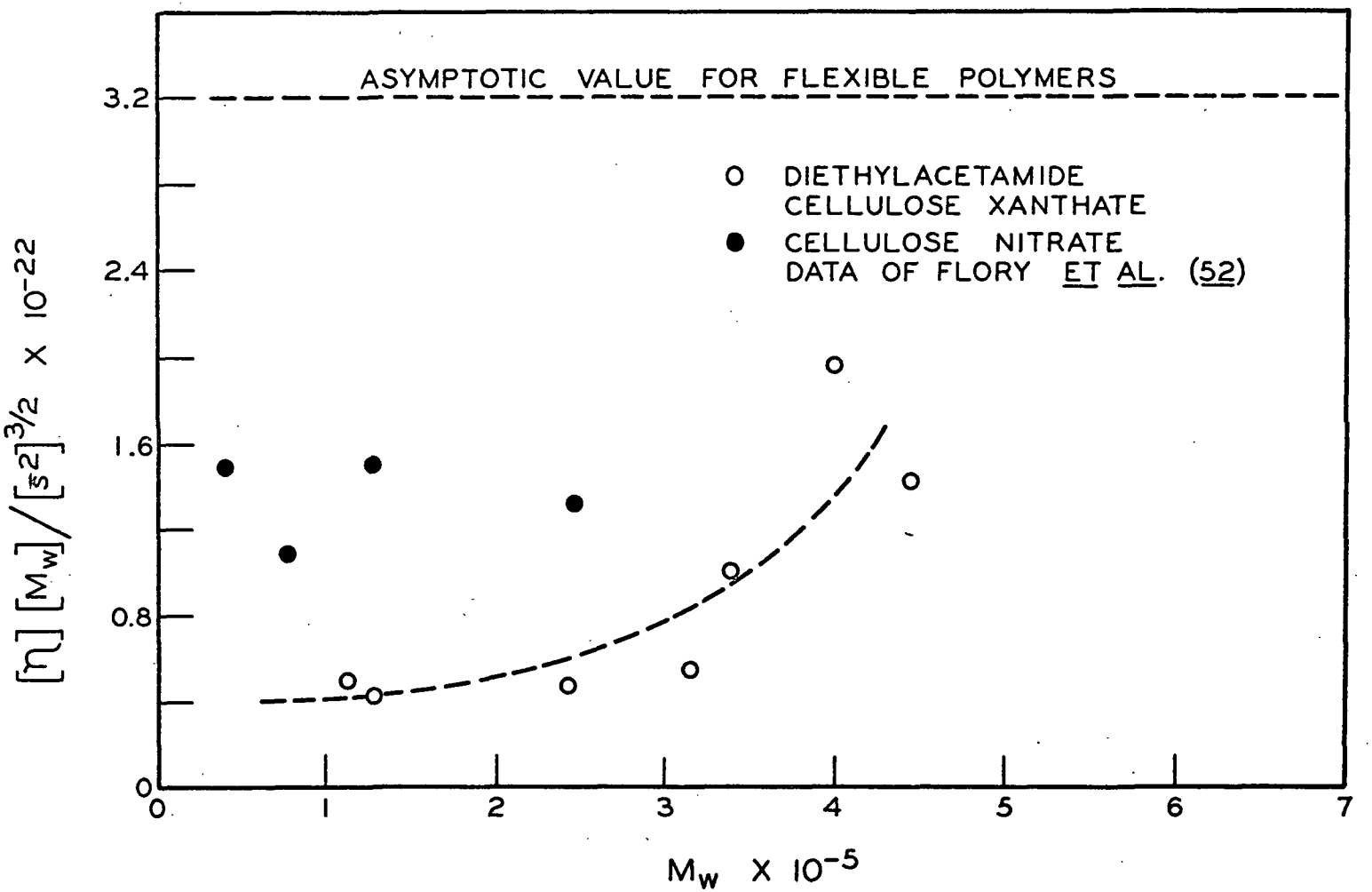

Figure 25. Variation of $[\eta][M_w]/(\bar{s}^2)^{3/2}$ with Molecular Weight (M_w)

TABLE XX

HYDRODYNAMIC PARAMETERS FOR DIETHYLACETAMIDE CELLULOSE XANTHATE IN 90% DIMETHYL SULFOXIDE

Sample	1	2	3	4	5	6	7
D.S.	0.40	0.49	0.60	0.80	0.92	1.00	1.22
$\underline{M}_w \times 10^{-5}$	1.12	1.29	3.16	2.45	4.01	3.40	4.46
$D.P._w$	473	506	1150	781	1190	969	1130
$[\eta]$	1.79	2.31	4.40	2.44	2.67	1.89	2.04
$[\eta]\underline{M}_w/(\underline{\bar{s}}^2)^{1/2} \times 10^{-22}$	0.46	0.40	0.55	0.45	1.95	1.00	1.42
Porod-Kratky units, $\underline{x}_w$	29.8	19.8	43.6	26.6	176	90.3	129
$\underline{a}_2$	0.10	0.14	0.07	0.11	0.02	0.03	0.02
q_{Φ} ($\underline{y} = 1$)	2.12	2.10	2.06	2.13	2.00	2.00	2.00
q_{Φ} ($\underline{y} = 2$)	1.70	1.64	1.63	1.70	1.63	1.62	1.63
$\{\Phi'\} \times 10^{-22}$ ($\underline{y} = 1$)	0.98	0.85	1.12	0.96	3.90	2.00	2.84
$\{\Phi'\} \times 10^{-22}$ ($\underline{y} = 2$)	0.79	0.66	0.89	0.77	3.18	1.62	2.32

The data presented here are insufficient to provide a complete interpretation of these effects, but even in the case of extensive studies with cellulose nitrate (52) it has been concluded that "existing theories fail to offer a self-consistent interpretation of the observed decreases in $\{\Phi'\}$ with decreasing molecular weight."

In light of the similarity in behavior in solution of cellulose nitrate and the acetamide derivative as indicated by hydrodynamic considerations, the initial assumption of a value of unity for the exponent a appears justified. It is suggested that the effect of D.S. upon this exponent exists principally in the value of a_3 as defined by Equation (25-iii).

SUMMARY

Light-scattering and viscosity measurements were obtained for seven fractions of the diethylacetamide derivative of cellulose xanthate (DAX) in 90% dimethyl sulfoxide. The degree of substitution (D.S.) range represented by these samples was 0.4 to 1.2; the molecular weight (M_w) range, 112,000 to 446,000.

Scattering intensities were determined at angles of 45, 90, and 135°, using an incident wavelength of 5461 A. The calculated turbidities were corrected for both depolarization and dissymmetry of the scattered light. Fluorescence effects were found to be negligible at this wavelength.

Consideration of the calculated configuration parameters led to the following results:

1. The molecular expansion factor, α, ranged from 1.01 to 1.12. There was some indication that α increased with molecular weight and/or D.S.

2. The unperturbed root mean square end-to-end length of the DAX molecule in solution ranged from 786 A. to 1520 A. The ratio of the end-to-end length to the contour length justified the initial assumption of a random coil configuration.

3. The unperturbed root mean square radius of gyration ranged from 319 A. to 631 A.

4. As with other cellulose derivatives, free rotation in solution was considerably hindered as indicated by the calculated effective bond length, the persistence length, and the $(\bar{r}_o^2/\bar{r}_{of}^2)^{1/2}$ ratio. The average effective bond length of 37 A. was comparable to the value of 35 A. reported for cellulose nitrate (78). The persistence length for the DAX derivative in the D.S. range 0.49 to 0.80 was 135 A. Flory, et al. (52) have reported a value of 117 A. for cellulose nitrate in ethyl acetate. The $(\bar{r}_o^2/\bar{r}_{of}^2)^{1/2}$ ratio ranged from 3.1 to 5.7, again comparable to values expected for cellulose derivatives.

Consideration of the hydrodynamic parameters led to the following results regarding the factors contributing to the exponent a in the modified Staudinger equation, $[\eta] = KM^a$:

1. The apparent increase in α with molecular weight resulted in an estimated exponent contribution of 0.02.

2. The effective contribution due to the departure of the chain configuration from random-flight behavior was 0.12, which corresponds to a value of 0.13 reported for cellulose nitrate (52).

3. The remaining contribution due to variation in the hydrodynamic parameter $\{\Phi'\}$ with molecular weight could not be evaluated from the data due to the concomitant effects of both D.P. and D.S. reflected in the calculated value of $\{\Phi'\}$. Indications were, however, that this contribution was quite large.

CONCLUSIONS

From this preliminary investigation of the solution properties of diethylacetamide cellulose xanthate in 90% dimethyl sulfoxide, it is possible to draw the following conclusions:

1. As reflected by the k_m-D.S. plot, the Martin constant, and the second virial coefficient, high-D.S. derivatives are more coiled in solution than low-D.S. derivatives of the same chain length.

2. The behavior of the DAX derivative in solution is strikingly similar to that of cellulose nitrate as indicated by the calculated effective bond length, the persistence length, $(\bar{r}_o^2/\bar{r}_{of}^2)^{1/2}$ ratio, and hydrodynamic parameters. The DAX molecule is considerably more extended than the common synthetic polymers due to effects of steric hindrance and the fixed valence angle. The behavior appears to approach that of the more flexible polymers at D.S. levels above 1.0 and molecular weights above 400,000.

3. Excluded volume and thermodynamic effects do not contribute significantly to the molecular weight-viscosity relationship. The effect due to deviations of the chain from random-flight behavior appears to be significant. This effect is dependent both on the D.S. and D.P. of the sample.

SUGGESTIONS FOR FUTURE WORK

1. There are certain inherent disadvantages in the use of the stable diethylacetamide derivative in investigations of this nature, namely with regard to its limited solubility. Other derivatives are readily prepared; however, there is little reference in the literature to the properties of such derivatives. It would be particularly advantageous in investigations of the early stages of the xanthation reaction to be able to prepare such derivatives which dissolve easily in suitable solvents.

2. There is little known regarding the transesterification of xanthate groups in viscose. It appeared from this work and other work reported in the literature (2, 5, 17, 39) that transesterification occurs rather rapidly. It has been suggested that equilibrium with regard to xanthate group distribution was attained within two hours for commercial cellulose xanthate (39). Mixtures of freshly prepared viscoses differing in D.S. would enable one to follow changes in the distribution of the substituents.

3. Further investigation of the solution properties of the diethylacetamide derivative would result in a more complete understanding of the effects of D.S. and D.P. on the configuration and hydrodynamic parameters. Using appropriate techniques, the molecular weight exponent of the Staudinger equation could readily be determined and the corresponding contributing factors evaluated. As indicated by Flory, et al. (52), considerably more data is required to reconcile the observed change in $\{\Phi'\}$ with molecular weight with the existing theories.

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APPENDIX I

EXPERIMENTAL METHODS

PREPARATION OF CELLULOSE NITRATE (49)

The cotton linters (1.0 gram) were cooled to -30°C. and 160 grams of the nitrating acid (nitric acid:acetic acid:acetic anhydride = 43:32:25) were added. The reaction mixture was placed in an ice bath for three hours and shaken occasionally. The nitrated cellulose was washed with ice water followed by stabilization with methanol.

NITROGEN DETERMINATION (1)

The sample to be analyzed (15-25 mg.), i.e., cellulose nitrate or diethylacetamide cellulose xanthate, was accurately weighed into a 30 ml. micro-Kjeldahl flask. Approximately 0.1 gram of reagent-grade salicylic acid and 2.0 ml. of concentrated sulfuric acid were added to the flask. The mixture was allowed to stand overnight or until solution was complete. Approximately 0.3 gram of analytical grade sodium thiosulfate and 0.6 gram of anhydrous potassium sulfate were added. A colorless solution, indicating complete digestion, was obtained by heating for six hours. The sample was washed into the distillation flask. Following addition of 20 ml. of 35% sodium hydroxide, the sample was distilled for five to seven minutes directly into a flask containing 25 ml. of 0.8% boric acid, previously made slightly acid against a mixed indicator of five parts of a 0.1% solution of brom cresol green and one part of a 0.1% solution of methyl red. The liberated ammonia was directly titrated with 0.01N hydrochloric acid, using a weight buret.

The method was standardized with a reagent-grade potassium nitrate and a standard cellulose nitrate, having nitrogen contents of 13.85 and 13.40%, respectively. A blank value of 0.285 ml. was found.

The nitrogen content was calculated from the following relationship:

$$\text{Nitrogen, } \% = (x)(y)(1.401)/w$$

where

x = the normality of the hydrochloric acid,

y = the ml. of hydrochloric acid needed for the titration, and

w = the sample weight.

CHEMICAL CHARACTERIZATION OF THE VISCOSE

Test Solution

To simplify sampling, a standard test solution (25 grams of viscose/250 ml.) was prepared by dilution of the viscose with distilled water. This solution was kept under refrigeration until the subsequent testing was complete.

Total Sulfur (as CS_2) (56)

Into a 500-ml. Erlenmeyer flask, 100 ml. of cold distilled water, 10 ml. of sodium zincate reagent[a], and a 10 ml. aliquot of the diluted viscose were introduced. After 30 minutes boiling, the contents of the flask were cooled in ice water and transferred to a 500-ml. flask containing a cold solution of M sulfuric acid and a known volume of 0.1N

[a] Sodium zincate reagent: 10 grams of zinc oxide plus 100 grams of sodium hydroxide diluted to 1000 ml. with distilled water.

iodine. A minimum of 20 minutes was necessary to decompose the zinc sulfide entirely. The unconsumed iodine was titrated with standard 0.1N sodium thiosulfate.

Total sulfur, % = 0.1903 x ml. 0.1N iodine consumed

Xanthate Sulfur (as CS_2): Ion-Exchange Method (37, 57, 58)

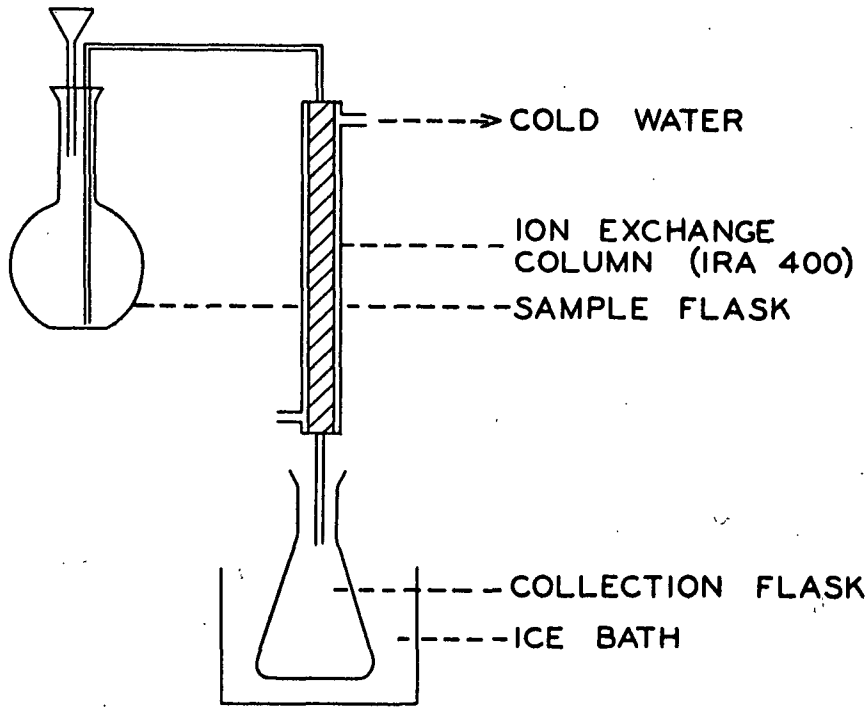

Figure 26. Ion-Exchange Apparatus for Xanthate Sulfur Determination

A 10-ml. aliquot of the viscose test solution was diluted with 100 ml. of cold distilled water and washed into the sample flask (Fig. 26). The solution was drawn through the ion-exchange column (Amberlite IRA 400) at a flow rate of 5-8 ml. per minute. The effluent was collected in a 500-ml. flask containing 10 ml. of sodium zincate reagent. The sample flask and column were washed by passing

an additional 100 ml. of ice water at the same flow rate. The combined filtrates were boiled for 30 minutes, cooled in ice water, and transferred to a 500-ml. flask containing 50 ml. of M sulfuric acid and 10 ml. of 0.1N iodine. After a minimum of 20 minutes reaction time the unconsumed iodine was titrated with 0.1N sodium thiosulfate.

$$\text{Rcell-OCS}_2\text{Na} + 2\text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{ZnS} + \text{Na}_2\text{CO}_3 + 3\text{NaOH} + \text{Rcell-OH}$$

$$2\text{ZnS} + \text{I}_2 \longrightarrow 2\text{S} + 2\text{Zn}^{++} + 2\text{I}^-$$

$$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$$

Xanthate sulfur, % = 0.1903 x ml. 0.1N iodine consumed

D.S. = 0.405 x ml. 0.1N iodine consumed/ per cent cellulose in viscose

By-Product Sulfur (as CS_2)

By-product sulfur, % = Total sulfur, % - Xanthate sulfur, %

Total Alkali (as NaOH) (59)

An aliquot (25 ml.) of the test solution was diluted with 30 ml. of distilled water, and 25 ml. of N sulfuric acid were added. The mixture was warmed for 15 minutes with constant shaking. The excess acid was neutralized to a phenolphthalein end point with N sodium hydroxide.

Total alkali, % = 4 x ml. N sulfuric acid consumed per gram of viscose

Free Alkali (as NaOH) (60)

An aliquot (50 ml.) of the test solution was diluted with 100 ml. of cold distilled water. To this solution was added sufficient saturated barium chloride solution to bring the total volume to 250 ml. The solution was allowed to sediment overnight under refrigeration. Fifty

milliliters of the clear solution were titrated with 0.1N sulfuric acid to a phenolphthalein end point.

$$\text{Free alkali, \%} = 0.4 \times \text{ml. 0.1N sulfuric acid consumed per gram of viscose}$$

By-Product NaOH (as NaOH)

$$\text{By-product NaOH, \%} = \text{Total alkali, \%} - \text{Free alkali, \%}$$

SOLUBLE CELLULOSE XANTHATE IN THE VISCOSE

Seventy-five grams (weighed to the nearest 0.1 gram) were diluted to approximately 500 ml. with 14% sodium hydroxide. The insoluble cellulose xanthate was separated by centrifuging for one hour at 1500 r.p.m. The residue was washed on to a previously tared filter, decomposed with 4N hydrochloric acid, and washed with distilled water. After a final washing with 95% ethanol, the sample was dried to constant weight at 105°C.

APPENDIX II

VISCOSITY DATA

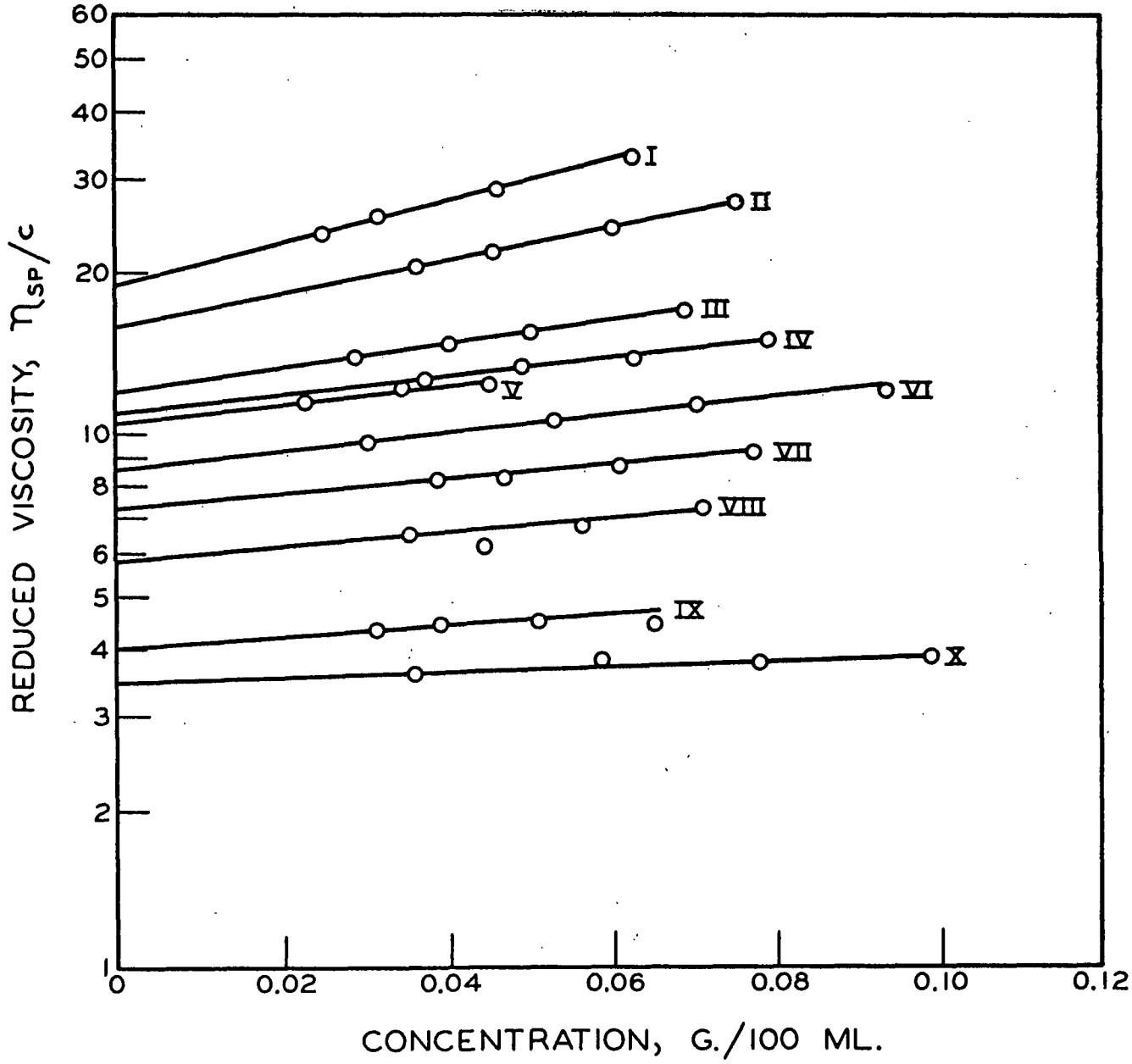

Figure 27. Viscosity Data--Nitrated Cotton Linters in Ethyl Acetate

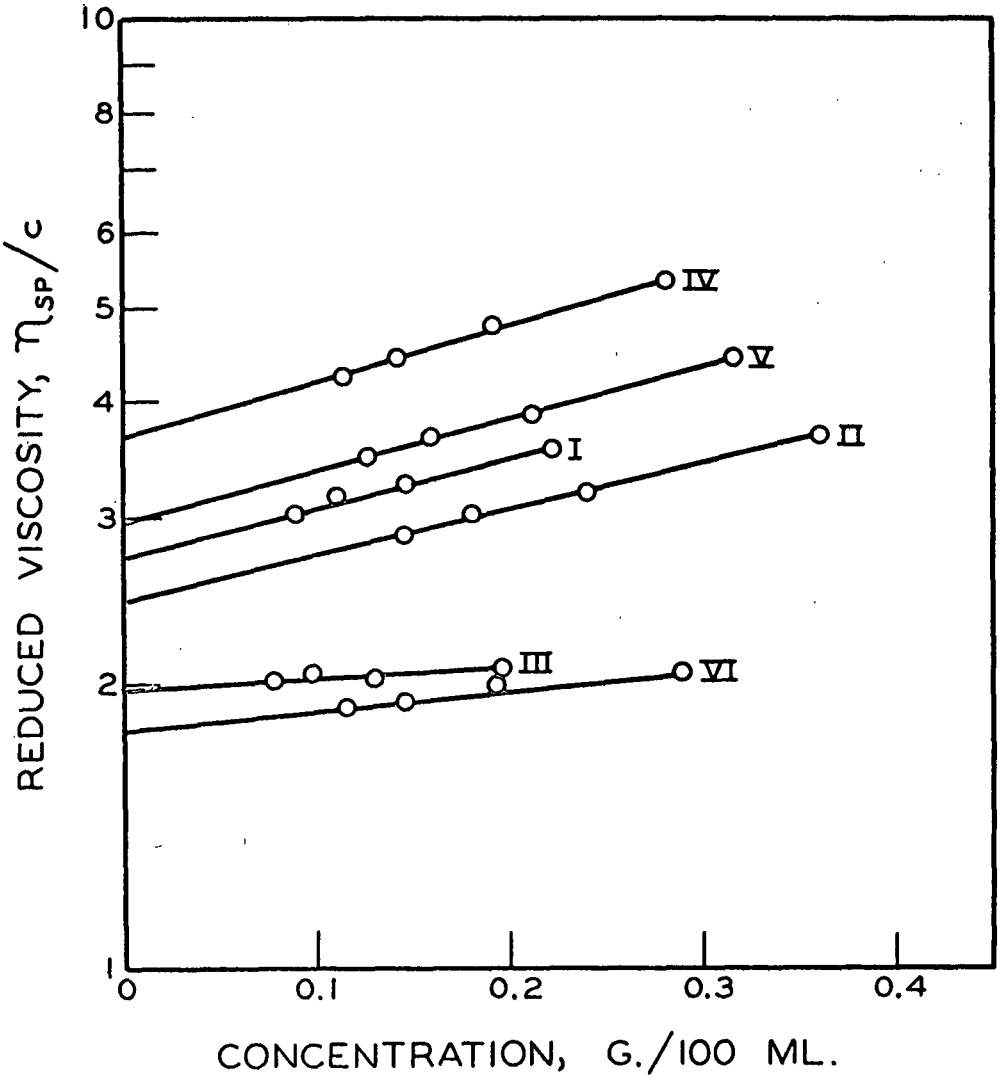

Figure 28. Viscosity Data--DAX A-E in 90% Dimethyl Sulfoxide

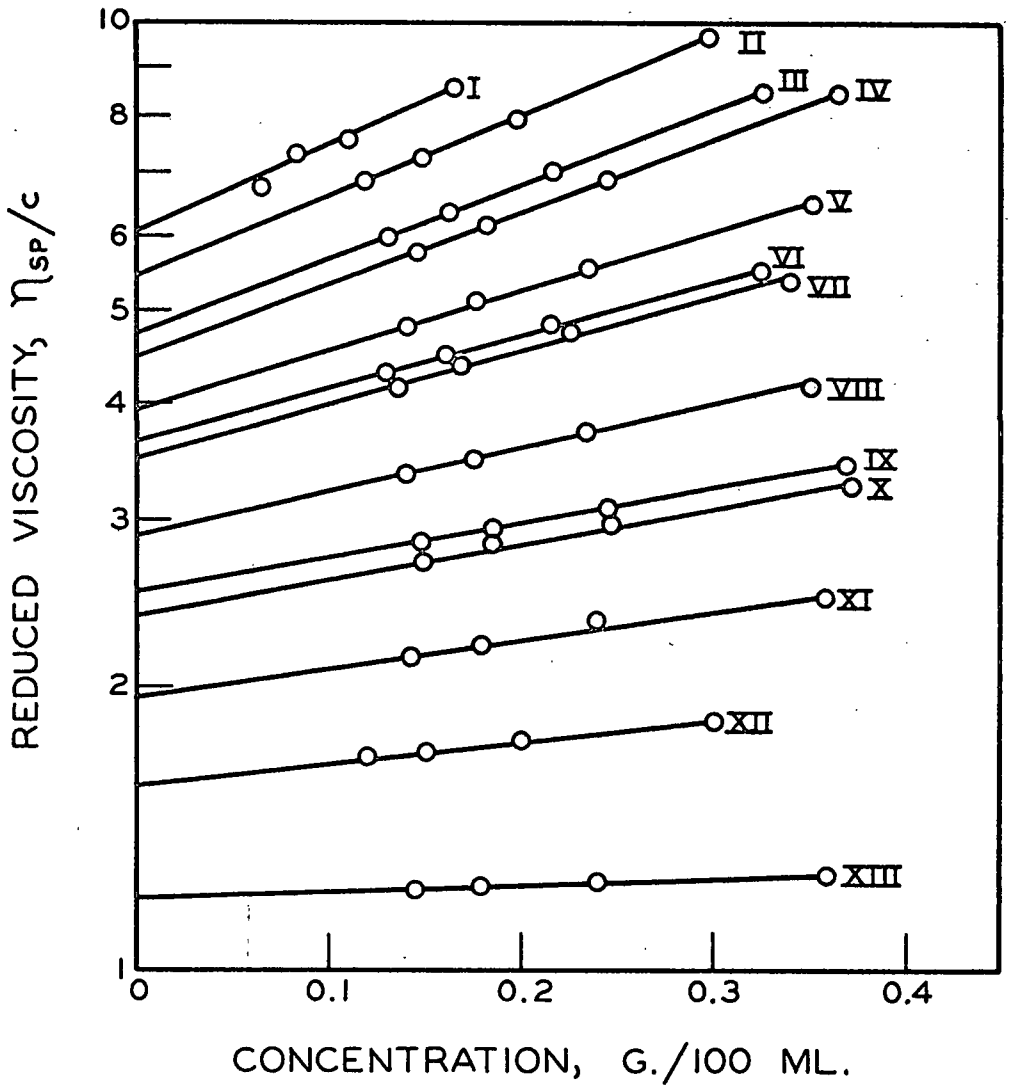

Figure 29. Viscosity Data--DAX A in 90% Dimethyl Sulfoxide

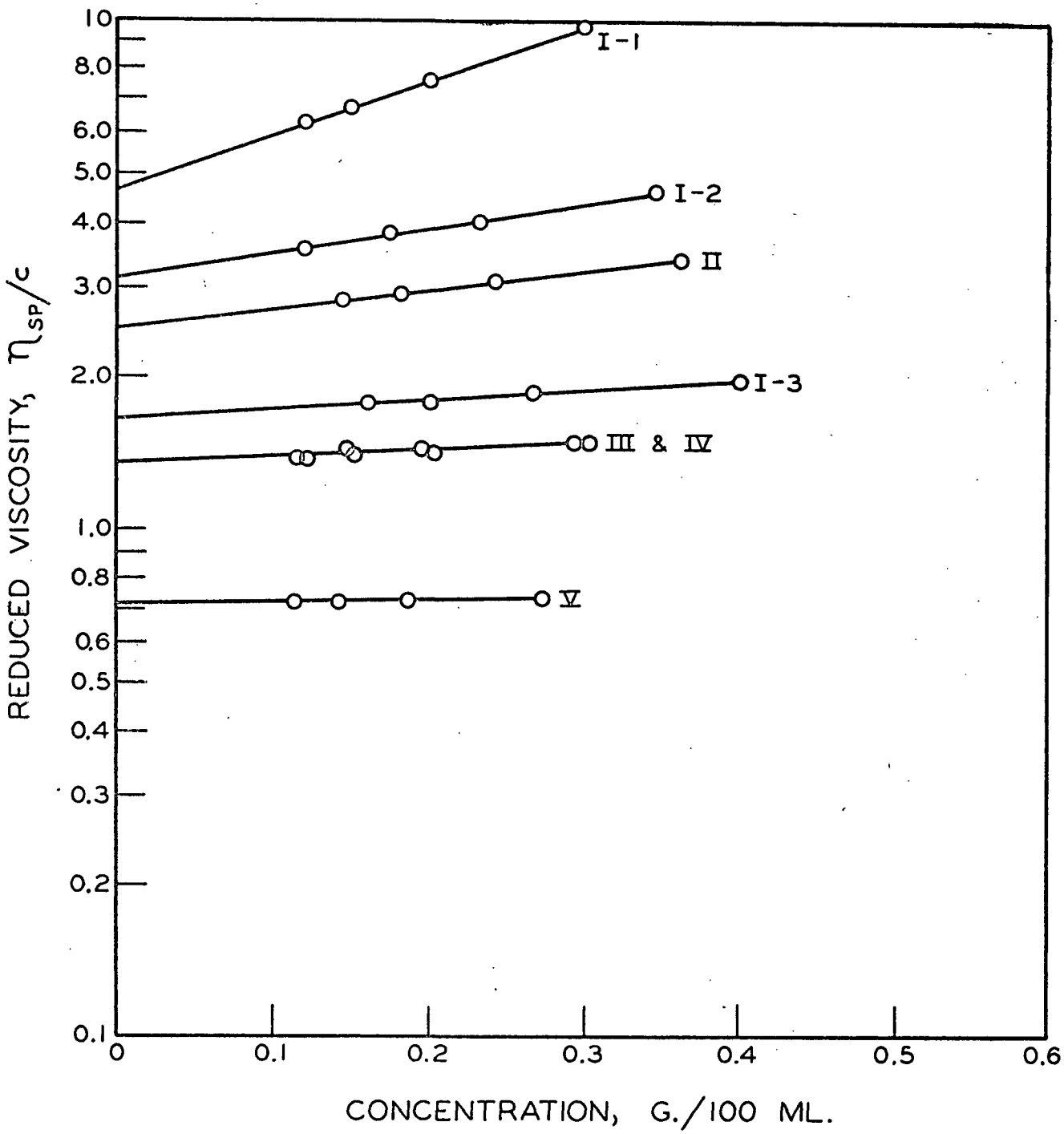

Figure 30. Viscosity Data--DAX B in 90% Dimethyl Sulfoxide

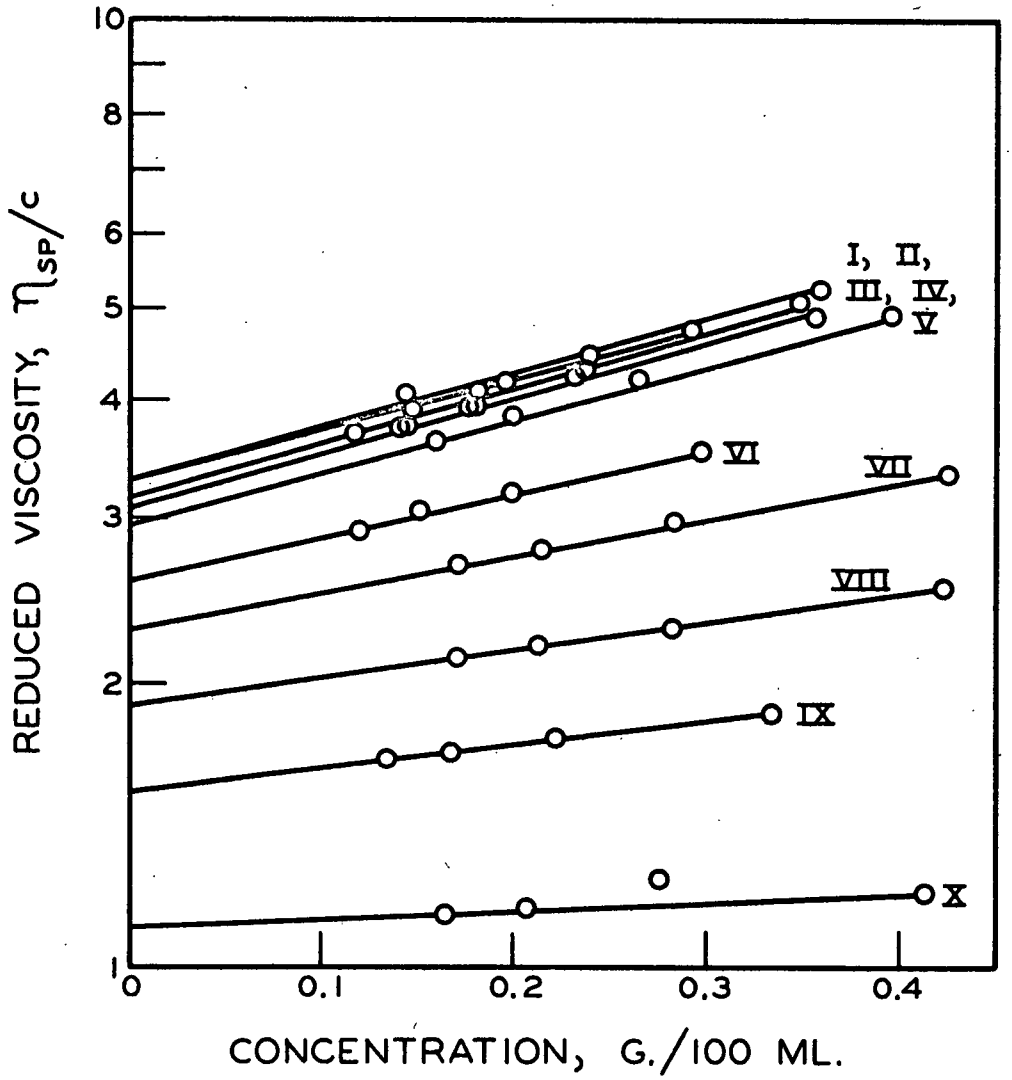

Figure 31. Viscosity Data--DAX C in 90% Dimethyl Sulfoxide

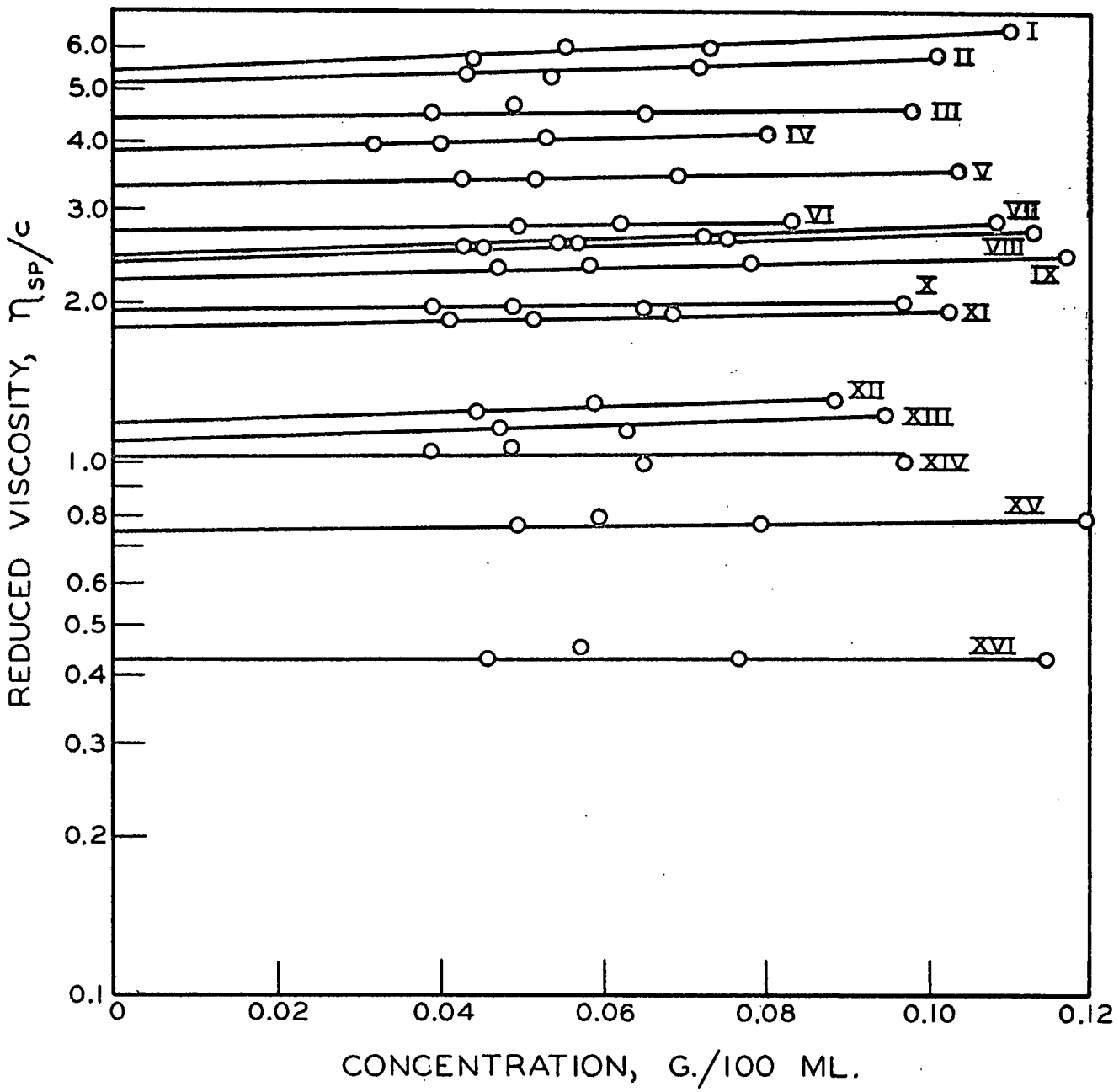

Figure 32. Viscosity Data--DAX D in 70% 2-Chloroethanol

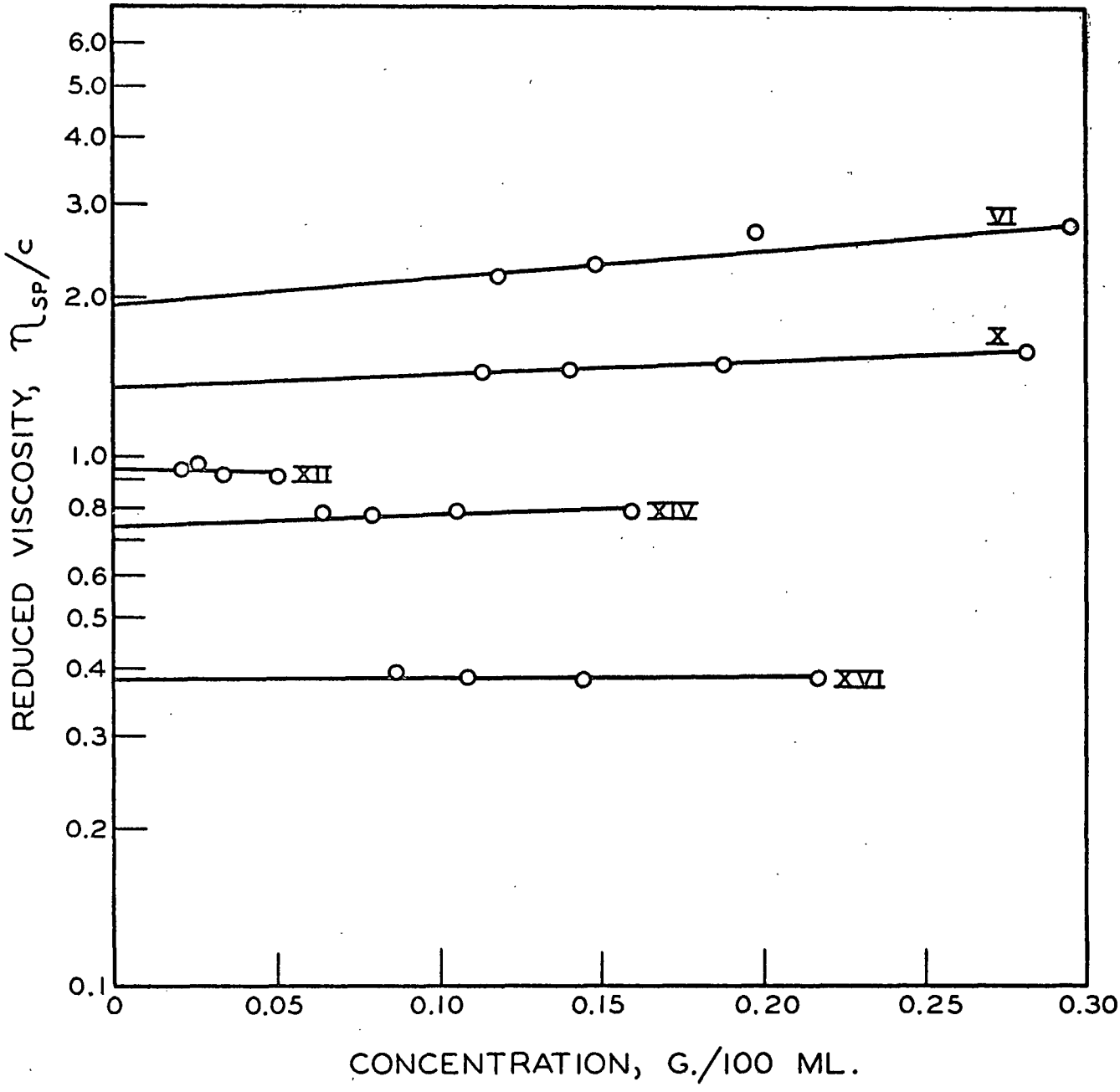

Figure 33. Viscosity Data--DAX D in 90% Dimethyl Sulfoxide

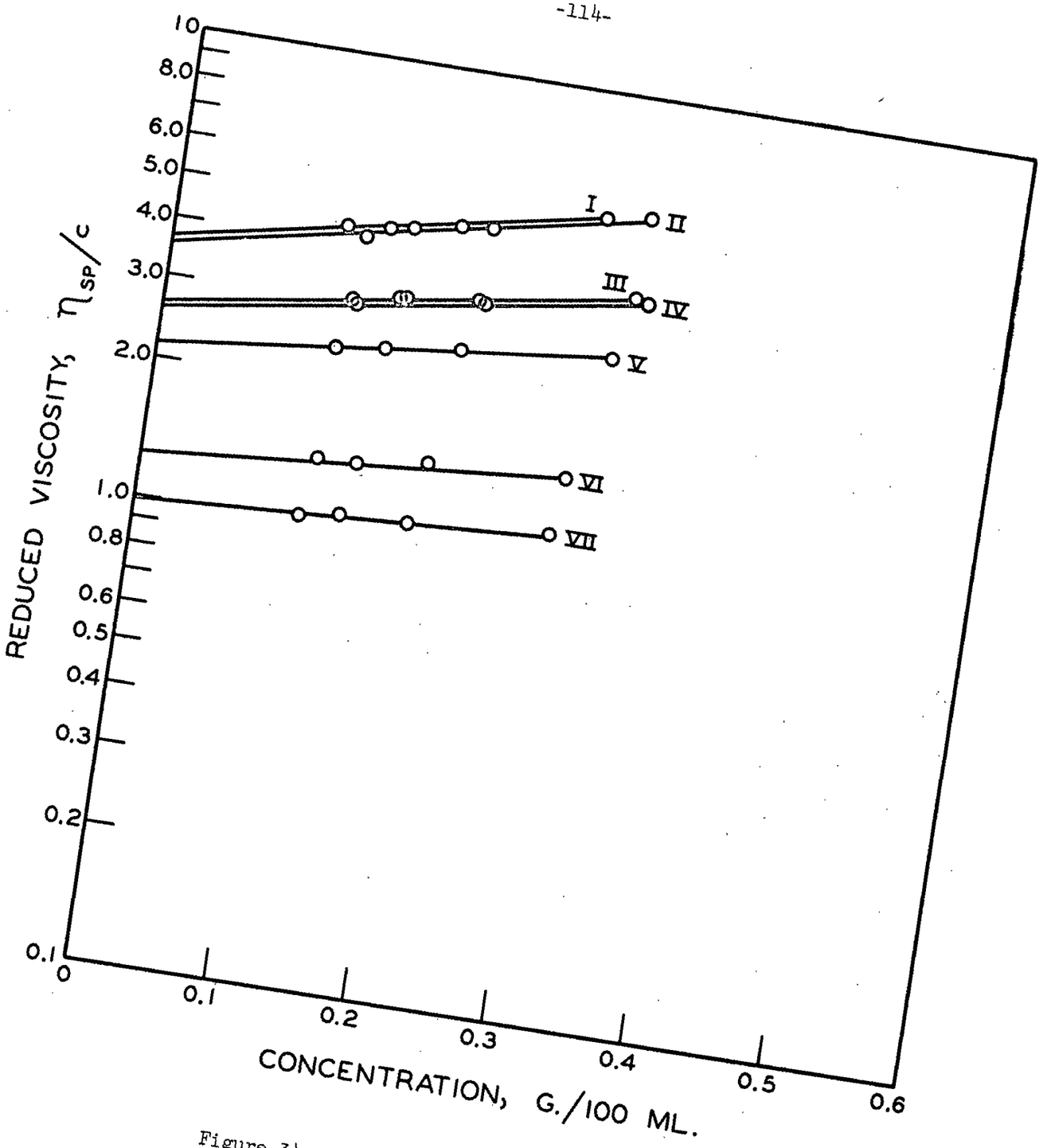

Figure 34. Viscosity Data--DAX B-3 in 90% Dimethyl Sulfoxide

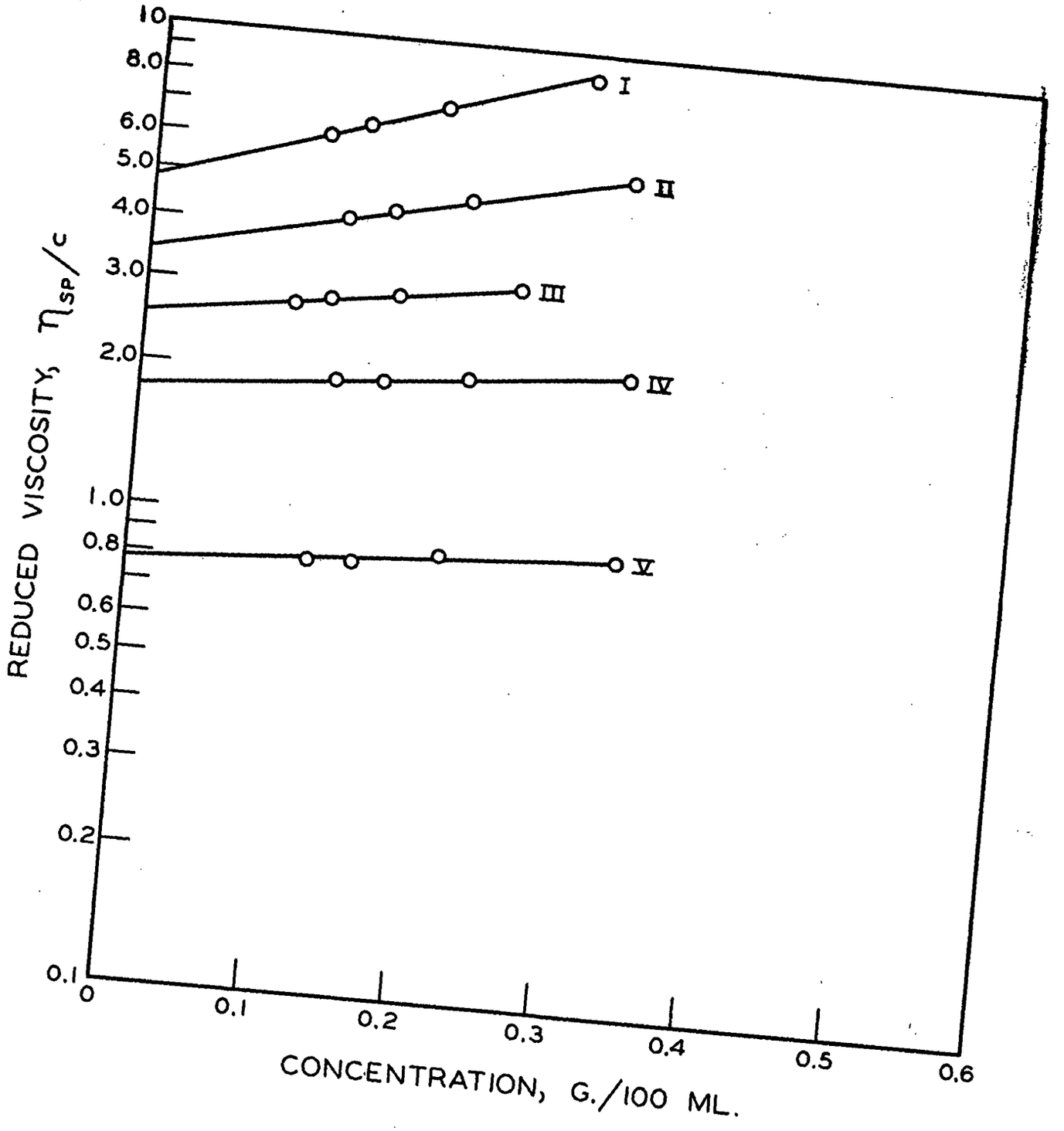

Figure 35. Viscosity Data--DAX B-4 in 90% Dimethyl Sulfoxide

APPENDIX III

TABLE XXI

REFRACTIVE INDEX DATA

Sample	Concn., g./ml. x 10^2	Drum Reading[a]	Fringe Displacement, $\underline{M}$[b]
1	0.289	406	7.78
	0.177	263	4.75
2	0.324	310	5.74
	0.264	268	4.85
3	0.206	293	5.39
	0.134	220	3.83
4	0.360	485	9.46
	0.199	296	5.44
	0.151	218	3.79
	0.122	180	2.98
5	0.244	251	4.27
6	0.393	362	6.85
	0.319	313	5.81
	0.268	257	4.62
7	0.360	283	5.17
	0.288	222	3.87
	0.232	195	3.08

[a] Arbitrary units on interferometer scale (47 units = 1 fringe).

[b] Calculated according to the following relationship:

$$\underline{M} = (\text{Drum Reading} - 40)/47$$

where the value 40 represents the drum reading with pure solvent in both cells. The refractive index gradient was calculated from this value of $\underline{M}$, according to Equation (7).

Note: As indicated in Fig. 36, there appears to be a decided decrease in $\underline{dn}/\underline{dc}$ with increasing D.S. Similar behavior has been noted by Badger and Blaker (74) for cellulose nitrate. The authors also found that $\underline{dn}/\underline{dc}$ was independent of molecular weight.

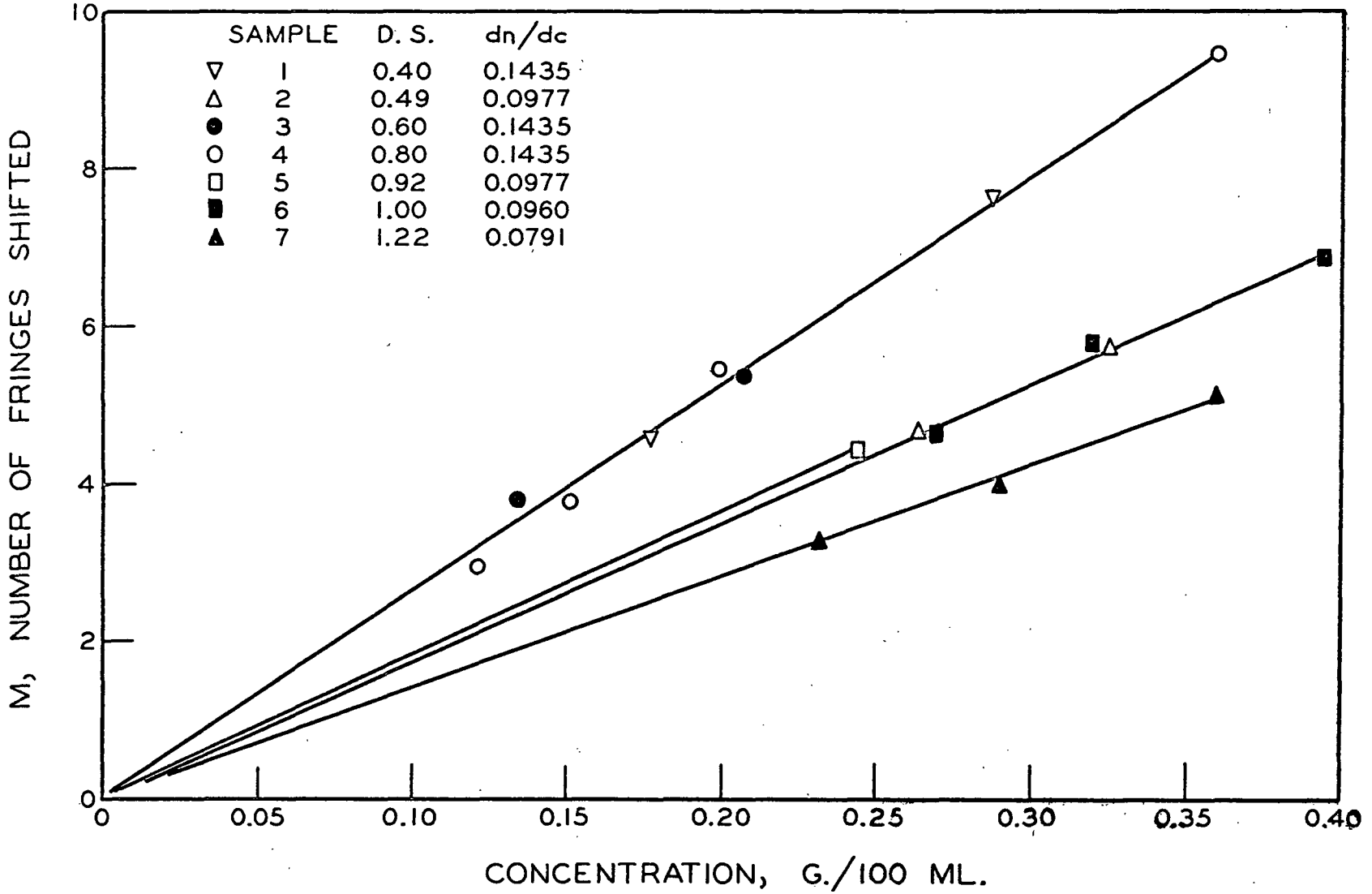

Figure 36. Refractive Index Gradients--Fractionated DAX Samples

APPENDIX IV

DISSYMMETRY AND DEPOLARIZATION MEASUREMENTS

Macromolecules in solution exhibit deviations from the generalized light-scattering equation represented in Equation (4), i.e., due to dissymmetry and depolarization of the scattered light.

In cases where the long dimension of the molecule exceeds $\lambda/20$ (where λ is the wavelength of the light in the solution), destructive interference occurs. The angular scattering is no longer symmetrical. The particle-scattering function, $\underline{P}(\theta)$, is introduced to account for this phenomenon.

$$\underline{Hc}/\tau \ (90°,0) = 1/\underline{M}_w \underline{P}(\theta)$$

The value of $\underline{P}(\theta)$ is obtained directly from the calculated limiting dissymmetry, $[\underline{Z}]$, using the tables of Doty and Steiner (88). The limiting dissymmetry was evaluated by determining the dissymmetry ratio, $\underline{R}(45)/\underline{R}(135)$, at various concentrations and extrapolating the $1/(\underline{Z}-1)$ ratio to zero concentration (87). The limiting dissymmetry obtained from this extrapolation was corrected for internally reflected light by means of the following relationship (101):

$$[\underline{Z}]_{corr} = ([\underline{Z}]_{obs} - \underline{R})/(1 - \underline{R}[\underline{Z}]_{obs})$$

where $\underline{R}$ is a function of the differences in refractive index at the interfaces of the light-scattering cell. For a glass-air interface, $\underline{R}$ is equal to 0.046 (85).

The dissymmetry data for the DAX fractions are summarized in Table XXII and are shown in Fig. 37.

TABLE XXII

DISSYMMETRY AND DEPOLARIZATION DATA

	Concn., g./ml. x 10^2	Z_{obs}	$1/(Z_{obs}-1)$	ρ_u	$(6+6\rho_u)/(6-7\rho_u)$
Sample 1	0.289 (0.044)[a]	1.289	3.46	0.076	1.18_1
D.S. = 0.40	0.224 (0.035)	1.274	3.65	0.073	1.17_3
	0.177 (0.028)	1.295	3.39	0.072	1.17_0
	0.149 (0.021)	1.295	3.39	0.071	1.16_7
Sample 2	0.324	1.460	2.18	--	--
D.S. = 0.49	0.264	1.446	2.24	--	--
	0.221	1.446	2.24	--	--
	0.188	1.455	2.20	--	--
	0.164	1.450	2.23	0.065	1.15_1
Sample 3	0.206	1.418	2.39	0.045	1.10_1
D.S. = 0.60	0.134	1.548	1.83	0.039	1.09_0
	0.117	1.578	1.73	0.028	1.06_2
	0.094	1.655	1.53	0.025	1.05_5
Sample 4	0.360	1.345	2.90	--	--
D.S. = 0.80	0.199	1.421	2.38	--	--
	0.151	1.483	2.07	--	--
	0.122	1.500	2.00	--	--
Sample 5	0.244	1.232	4.31	--	--
D.S. = 0.92	0.199	1.248	4.03	--	--
	0.171	1.283	3.53	--	--
Sample 6	0.393	1.357	2.80	0.059	1.13_5
D.S. = 1.00	0.320	1.373	2.68	0.057	1.13_2
	0.268	1.379	2.64	0.056	1.12_8
	0.223	1.382	2.62	0.052	1.12_2
Sample 7	0.360	1.356	2.81	0.037	1.08_3
D.S. = 1.22	0.288	1.375	2.67	0.030	1.06_8
	0.232	1.376	2.66	0.024	1.05_3
	0.184	1.382	2.62	0.017	1.03_7

[a] Concentrations used for depolarization measurements.

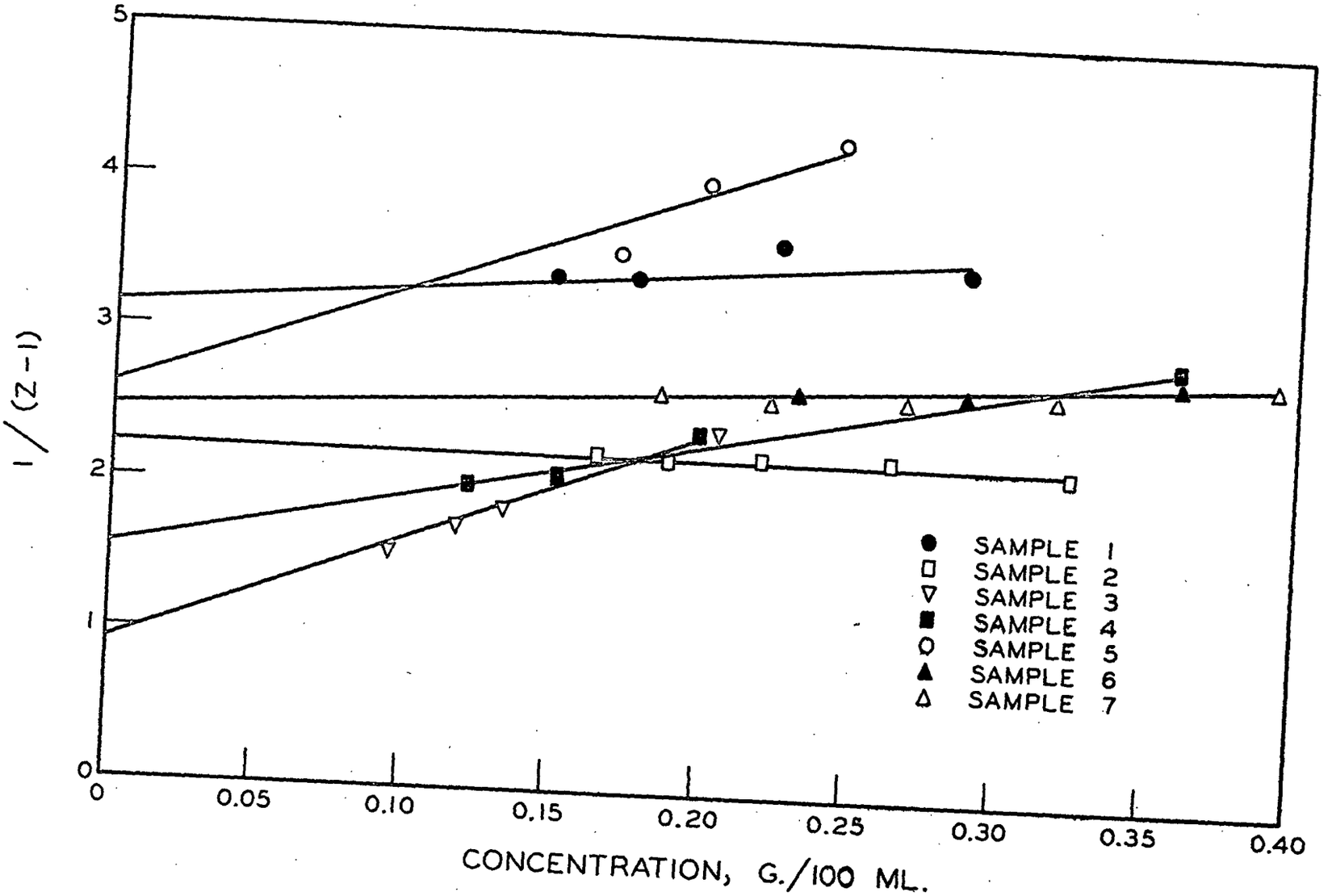

Figure 37. Dissymmetry Measurements--Fractionated DAX Samples

Light scattered transversely by anisotropic molecules in solution will no longer be plane polarized but will be augmented by an additional horizontal component. The measured scattering will, therefore, be greater than that exhibited by isotropic molecules of the same size. The correction for this effect is expressed by the ratio $(6 - 7\rho_u)/(6 + 6\rho_u)$, where ρ_u is the ratio of the horizontal component measured at 90° to the vertical component for unpolarized incident light (89).

The depolarization ρ_u was determined in the following manner: With cell removed from the cell table, the sensitivity adjustment was set to give a reading of 95 on the galvanometer scale for the transmitted beam with the polaroid analyzer in the horizontal position. Readings were taken at several concentrations for both the horizontal and vertical components at an angle of 90°. In this manner it was possible to obtain the depolarization measurements in conjunction with the other light-scattering measurements.

The depolarization data are summarized in Table XXII and are shown graphically in Fig. 38.

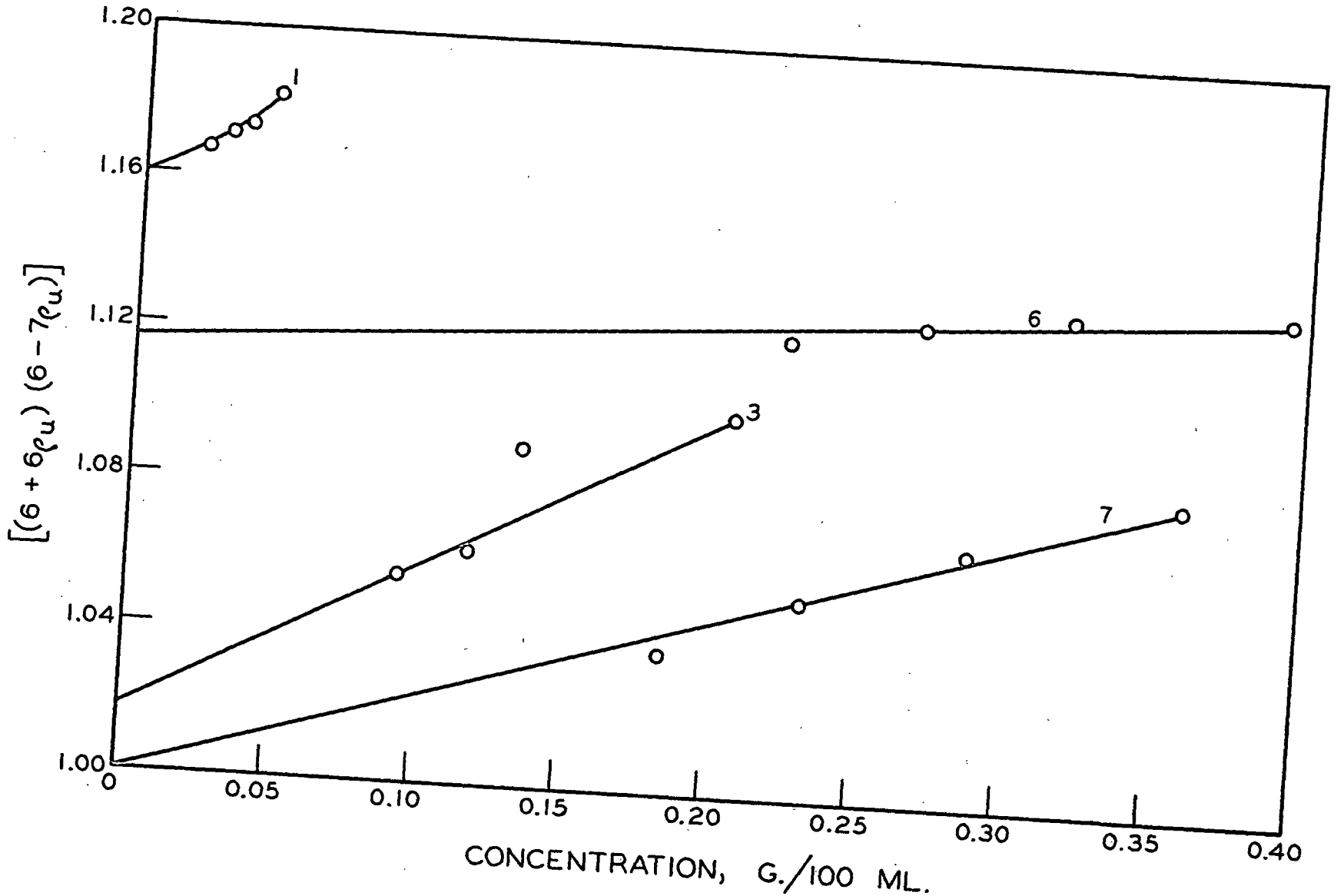

Figure 38. Depolarization Measurements--Fractionated DAX Samples